

ECSCD-12

European Conference on Surface Crystallography and Dynamics

18-21 October 2015
Trieste, Italy

Book of Abstracts



Scope

The European Conference on Surface Crystallography and Dynamics (ECSCD) addresses the atomic-scale characterization of surface structure and its relation to dynamics. The main focus is the precise determination of atomic positions in systems of increasing complexity, carried out by means of experimental and computational methods. Topics include a wide range of processes (adatom and molecule diffusion, surface stress, surface thermodynamics, self-assembled systems, and magnetism) occurring at the surfaces of different materials (metals, alloys, oxides, nanostructures, clusters, complex and smart materials). Methods may span from surface science in vacuum to novel approaches focused on bridging pressure and material gaps, towards in situ and in operando studies with time and/or spatial resolution. The conference aims at providing a forum where highly reputed invited speakers and younger researchers can exchange knowledge and discuss the most recent theoretical and experimental developments in surface crystallography.

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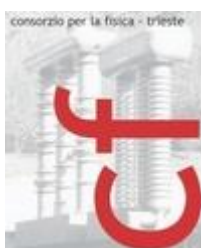
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ECSCD-12
**European Conference on Surface
Crystallography and Dynamics**

Scientific Program

Monday 19 October 2015

Morning - Session 1.1		
8:50 – 9:00	<i>Opening Remarks</i>	
9:00 – 9:40 Keynote Lecture	L. Hammer (Uni. Erlangen)	Oxide surfaces and surfaces oxides - structural complexity and surprises revealed by LEED intensity analyses
9:40 – 10:10 Invited Lecture	N. Seriani (ICTP, Trieste)	Structure of hematite(0001) and water splitting mechanism from ab-initio simulations
10:10 – 10:30	J. De la Figuera (CSIC, Madrid)	When shape lies: stacking fault removal on FeO growth on Ru(0001)
10:30 – 10:50	E. Lundgren (Lund University)	Substrate dependent reactivity of FeO ultra-thin films
<i>Coffee Break</i>		
Morning – Session 1.2		
11:20 – 11:50 Invited Lecture	C. Di Valentin (Uni. Milano-Bicocca)	Oxygen at Graphene/Cu(111) and Graphene/TiO ₂ (101) Interfaces: a Van der Waals DFT Study
11:50 – 12:20 Invited Lecture	J. Gustafson (Lund University)	In situ surface structure determination during catalytic reactions using high-energy surface X-ray diffraction
12:20 – 12:40	J.E. Ortega (Uni. Del Pais Basco, San Sebastian)	Revisiting old and exploring new surface science with curved crystals: Pt and TiO ₂
12:40 – 13:00	J.I. Flege (Uni. Bremen)	Nanoscale Origin of Mesoscale Roughening in Ruthenium Oxidation by O ₂
<i>Lunch</i>		
Afternoon – Session 1.3		
14:20 – 15:00 Keynote Lecture	B. Hammer (Uni. Aarhus)	Automated surface structure determination with DFT
15:00 – 15:20	X. Hu (Uni. Oxford)	Surface Structures of Ultrathin Ti ₂ O ₃ Films on Au(111)
15:20 – 15:40	A. Verdini (CNR-IOM, Trieste)	The influence of Mg of the surface properties in rutile TiO ₂ (011)
15:40 – 16:00	S. Agnoli (Uni. Padova)	The oxide-oxide interface in reducible oxides: a new paradigm in nanocatalysis
<i>Coffee Break</i>		
Afternoon – Session 1.4		
16:30 – 17:00 Invited Lecture	R.J. Maurer (Uni. Yale)	Finite-Temperature Effects on Structure and Energetics: Organic Adsorbates from a First-Principles Perspective
17:00 – 17:30 Invited Lecture	V.J. Bukas (TU München)	“Hot” adatoms hopping: Phononic dissipation & equilibration dynamics from first-principles
17:30 – 17:50	S.Y. Guo (Uni. Toronto)	Dynamics of Repulsion-Induced Surface-Migration by Ballistics and Bounce
18:00 – 19:30	<i>Poster Session</i>	

Tuesday 20 October 2015

Morning - Session 2.1		
9:00 – 9:40 Keynote Lecture	J.V. Barth (TU München)	Pathways to complex interfacial networks and 2D tessellations
9:40 – 10:10 Invited Lecture	P. Jelinek (AS CR, Prague)	What can we learn from high-resolution AFM/STM images: mapping molecular electrostatic potential
10:10 – 10:30	F.S. Tautz (PGI-3, Jülich)	Taking a stand: aromatic molecules in vertical adsorption geometries
10:30 – 10:50	O. Lytken (Uni. Erlangen)	Anhydride and Polyanhydride Formation By Phthalic Acid on Ag(100)
<i>Coffee Break</i>		
Morning – Session 2.2		
11:20 – 11:50 Invited Lecture	F.J. Giessibl (Uni. Regensburg)	Hot spots in atomic force microscopy
11:50 – 12:20 Invited Lecture	M.C. Tringides (Iowa State University)	Metal growth on graphene: morphology, intercalation and magnetization
12:20 – 12:40	J. Falta (Uni. Bremen)	Microspectroscopy and micro-diffraction analysis of transient, nanoscale cerium oxide phases during reduction by molecular hydrogen
12:40 – 13:00	M. Klimczak (FAU, Erlangen)	Structures, Interactions and Dynamics of Alkylimidazolium Ionic Liquids at the solid–liquid interface
<i>Lunch</i>		
Afternoon – Session 2.3		
14:20 – 15:00 Keynote Lecture	J.C. Meyer (Uni. Vienna)	Exploring 2D materials via high-resolution electron and scanned probe microscopies
15:00 – 15:20	D.A. Duncan (TUM, Munich)	A joint DFT and XSW study in to the “surface trans-effect”: If it looks like a duck, swims like a duck and quacks like a duck, is it actually a trans-effect?
15:20 – 15:40	K. Sotthewes (Uni. Twente)	Dynamics of copper-phthalocyanine in the molecular bridge position
15:40 – 16:00	D.P. Woodruff (Imperial College, London)	Ordered growth of vanadyl phthalocyanine (VOPc) on an iron phthalocyanine (FePc) monolayer: local V=O-Fe bonding?
<i>Coffee Break</i>		
Afternoon – Session 2.4		
16:30 – 17:00 Invited Lecture	M. Peressi (Uni. Trieste)	Surface structure and morphology of bimetallic alloys and nanoalloys: insights from numerical simulations
17:00 – 17:30 Invited Lecture	T.O. Mendes (Elettra, Trieste)	Structure and phase separation in ultrathin bimetallic alloys
17:30 – 17:50	M. Blanco-Rey (Uni. del Pais Vasco, San Sebastian)	Modelling of STM-induced diffusion of hydrogen interstitials in the Pd(111) near-surface region
18:30 – 20:00 20:30 -	<i>Visit to Elettra Social Dinner</i>	

Wednesday 21 October 2015

Morning - Session 3.1		
9:00 – 9:40 Keynote Lecture	M.S. Altman (Uni. Science and Technology, Hong Kong)	Structure and dynamics of two-dimensional layers with low energy electron microscopy and nano-diffraction
9:40 – 10:10 Invited Lecture	M. Stöhr (Uni. Groningen)	Comparing graphene growth on Cu(111) vs. oxidized Cu(111)
10:10 – 10:30	L.L. Patera (Uni. Trieste)	Fast STM observations of catalytic surface reactions: CVD graphene growth on Ni
10:30 – 10:50	P. Ferstl (Uni. Erlangen)	Atomic structure of one-dimensional metal-oxide hybrid chains formed on the Ir(100) surface
<i>Coffee Break</i>		
Morning – Session 3.2		
11:20 – 11:50 Invited Lecture	J.A. Martín-Gago (ICMM-CSIC, Madrid)	Structure of Epitaxial graphene Moiré coincidence network; lattice mismatch versus surface strain
11:50 – 12:20 Invited Lecture	S. Günther (TUM, München)	Moiré patterns formed by hexagonal coincidence lattices: applications for metal supported graphene and related materials
12:20 – 12:40	K. Hermann (FHI, MPG, Berlin)	Theory of Moiré Patterns Found for Graphene and Other Overlayers at Metal Surfaces
12:40 – 13:00	D. Menzel (TUM, München)	Ultrafast charge transfer at boron nitride monolayers on variably coupled substrates
<i>Concluding Remarks and Lunch</i>		

**ECSCD-12 Abstracts:
keynote lectures, invited talks and
oral presentations**

Oxide surfaces and surfaces oxides - structural complexity and surprises revealed by LEED intensity analyses

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The surfaces of transition metal oxides are quite often not just bulk-like terminated but chemically and geometrically reconstructed. There can be vacancies within either the oxygen or cation lattice as well as site switches towards interstitial position. These processes are not restricted to the very surface but can also occur - even exclusively - within subsurface layers as e.g. in the cases of $\text{Fe}_3\text{O}_4(100)$ [1] and $\text{CoO}(111)$ [2] and by that remain largely hidden to imaging methods like STM. For ultra-thin oxide films grown on reactive substrates the situation further complicates by the competition of binding forces within the film and towards the substrate [3]. This may even lead to Moire-type films with a laterally modulated structure as found for a $\text{CoO}(111)$ -type bilayer on $\text{Ir}(100)$ [4]. Modification of the substrate interaction - here by a pseudomorphic buffer layer of metallic cobalt - leads instead to a $\text{CoO}(100)$ -type layer with $c(4\times 2)$ -ordered Co-vacancies. These interface-driven structures also determine the growth orientation for thicker films [5]. In the sub-monolayer regime there is a further competition between 2D-oxide island growth and 1D-nanostructure formation. On the plain $\text{Ir}(100)$ surface for example, linear metal-oxide hybrid structures with CoO_2 and CoO_3 stoichiometry develop self-organised in threefold lateral distance, inducing a missing row substrate reconstruction below.

As demonstrated above, the structural solutions of nature for oxide surfaces and films are often complex and rather surprising, which makes the initial guess of the correct structure - the inevitable starting point of every structure determination - a demanding task. This is the more crucial the larger the surface unit cell becomes, since in such a case the contribution of one extra (or missing) atom alters the total wave field only moderately. This means that neglecting such an element in the model structure will also not lead to dramatic changes in the intensity spectra and so still seemingly plausible fits may result. As an example, LEED-IV analyses for the $c(2\times 2)$ -reconstructed surface of $\text{Fe}_3\text{O}_4(100)$ using models neglecting either the Fe vacancies or the interstitial ion still produce "best-fit" Pendry R-factors in the range 0.2 - 0.3, which are commonly called "acceptable fits"! As a consequence it has to be pointed out that trustworthy LEED fits in particular for complex structures have to be of significantly better quality ($R_p < 0.15$). To achieve this objective, large experimental and computational efforts are necessary: On the one hand, surface preparation has to be controlled and optimised preferably by local probes like STM in order to minimise structural defects and phase coexistence. On the other hand, also minute atomic relaxations have to be fitted and this can only be performed on the basis of huge data sets with large redundancy factors. And as a final proof, the derived structural parameters should be compared with those of a corresponding, fully relaxed total-energy calculation and coincide on a level below 0.1 Å.

References :

- [1] R. Bliem *et al.*, Science 346 (2014) 1215.
- [2] W. Meyer *et al.*, PRL 101 (2008) 016103.
- [3] K. Heinz and L. Hammer, JPCM 25 (2013) 173001.
- [4] C. Ebensperger *et al.*, PRB 81 (2010) 235405; C. Tröppner *et al.*, PRB 86 (2012) 235407.
- [5] M. Gubo *et al.*, PRL 108 (2012) 066101.

Structure of hematite(0001) and water splitting mechanism from ab-initio simulations

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Hematite has recently raised considerable interest as a possible photocatalyst for water oxidation. Despite the on-going research efforts, its efficiency is still unsatisfactory. To understand the behaviour of the (0001) surface of hematite in a realistic environment, we have performed first-principles simulations based on density functional theory. By taking into account the presence of water and oxygen under illumination, we show that the thermodynamically stable termination under reaction conditions is oxygen rich. On this termination, water oxidation proceeds by nucleophilic attack with an overpotential of 0.84 V. Finally, we have considered the possible effect of surface modifications such as impurities and ultrathin films on the properties of the surface. Nitrogen doping lowers the over-potential, while detrimental surface states disappear in presence of ultrathin films of gallium oxide or aluminium oxide. I am going to compare calculations with available experiments, and to discuss open questions and future developments in this field.

When shape lies: stacking fault removal on FeO growth on Ru(0001)

Matteo Monti¹, Laura Martín-García¹, Raquel Gargallo-Caballero¹, Michael Foerster², Lucia Aballe², and Juan de la Figuera¹

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The shape of a 2-dimensional island for fcc or hcp-based lattices growing on three-fold symmetry substrates is often determined by kinetic limitations, giving rise to triangular islands. Systems as diverse as Pt/Pt(111), Co/Ru(0001) or FeO/Au(111) follow this rule. But it has long been known that stacking faults or twins can be produced during growth. Such stacking faults or twins give rise to triangular islands with different orientations on a single substrate terrace. In fact, the presence of different orientations is usually taken as a proof of islands with different absorption sites, or for multilayer islands, different stacking sequences as in the pioneering work of Bethge on Ag/Au(111) [1]. In particular cases, the assumption has been confirmed by selected area diffraction or STM such as in Co/Ru(0001) [2]. But stacking faults can be removed during growth [3]. In this work we present results on the growth of FeO on Ru(0001) [4] where island shape is shown to be an unreliable indicator of stacking sequence. In this case, shape points to islands that had at some point a stacking fault, but which at other times have the same stacking as their non-rotated counterparts.

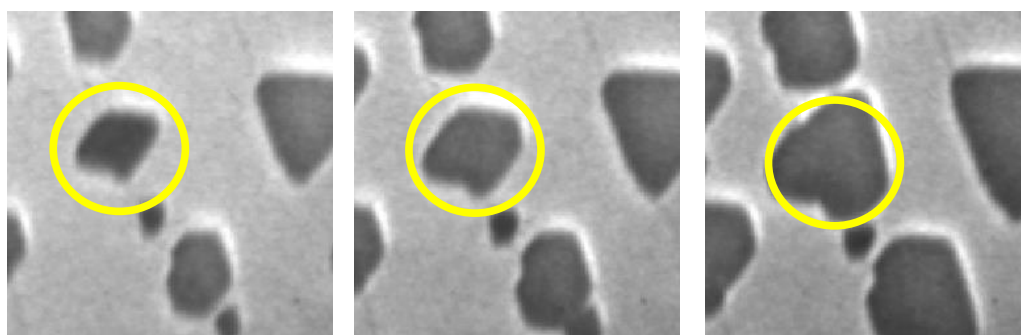


Figure 1: LEEM image of a growing FeO film. Marked with a yellow circle is an island whose stacking (identified by its different gray level) changes upon further growth. When growing even more FeO, the shape reverses. The image area are 2.5 μm wide.

References:

- [1] K. Meinel, M. Klaua, and H. Bethge. *Phys. Stat. Sol. (a)* **110**, 189–196 (1988).
- [2] F. El Gabaly et al., *New J. Phys.* **9**, 80 (2007).
- [3] C. Busse and T. Michely, *Surf. Sci.* **552**, 281–93 (2004); W.L. Ling et al., *Phys. Rev. Lett.* **95**, 166105 (2005).
- [4] I. Palacio et al., *J. Phys: Condens. Matter.* **25**, 484001 (2013).

Substrate dependent reactivity of FeO ultra-thin films

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Recently, monolayer-thick FeO films have gained significant attention in surface chemistry and catalysis. In particular FeO films grown on the Pt(111) surface have been studied in detail [1-4] and it has been reported, most intriguingly, that the formation of an O-Fe-O trilayer phase displays a higher activity than the Pt(111) surface itself for CO oxidation under semi-realistic conditions [4]. It has been suggested that, due to the loosely bound top-most oxygen atoms in the O-Fe-O layer, the reaction proceeds via an Eley-Rideal mechanism; The CO solely interacts with the top-most oxygen forming CO₂.

With the aim of elucidating the effects of the substrate on the chemical properties of ultra-thin FeO films, we have investigated the growth of FeO on Ag(100) as well as the reactivity of the FeO film towards NO adsorption. We present a detailed structural study of the growth of FeO ultra-thin films on the Ag(100) surface combining STM, LEED, XPS, NEXAFS and DFT calculations. We show that it is possible to produce a well-ordered FeO(111)-type monolayer on an Ag(100) surface by reactive deposition and annealing. The monolayer structure is expanded laterally compared to similar films grown on Pt surfaces, which is attributed to weaker interactions with the substrate. By varying the substrate temperature and the oxygen pressure, we show that it is also possible to grow FeO(100) grains and multilayer Fe and O layers [5].

Armed with this structural information we have studied the NO adsorption and desorption on the FeO ultra-thin films on Ag(100) using LEED, IRAS and TPD and compare the adsorption properties with those found for FeO films on Pt(111). Previous studies have shown that while a significant amount of NO adsorb on Pt(111), only a fraction adsorb on the FeO(111)/Pt(111), which has been attributed to NO adsorption on defects on the FeO(111) film [6]. In the case of the FeO(111)/Ag(100) the situation is reversed, revealing no NO adsorption on the Ag(100) at 85 K while almost a full monolayer adsorb on the FeO(111)/Ag(100) system. Thus, despite their clear structural resemblance, the FeO(111) films on Pt(111) and Ag(100) has completely different reactivity towards NO adsorption. The reasons for these differences will be discussed in the contribution.

References:

- [1] L. Giordano et al., J. Phys. Chem. C **114**, 21504 (2010).
- [2] H. Zeuthen et al., J. Phys. Chem. C **117**, 15155 (2013).
- [3] L. Giordano et al., Phys. Rev. B **76**, 75416 (2007).
- [4] J. Goniakowski, and C. Noguera, Phys. Rev. B **79**, 155433 (2009).
- [5] L. R. Merte et al, J. Chem Phys. C J. Chem. Phys. C **119** (2015) 2572.
- [6] Lei et al. ChemCatChem **3**, 671 (2011).

Oxygen at Graphene/Cu(111) and Graphene/TiO₂(101) Interfaces: a Van der Waals DFT Study

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The observation of an enhanced chemical reactivity at graphene/support interfaces is currently a hot topic of research and it is rationalized as the consequence of the two-dimensional confinement effect. In this context we have investigated, by means of density functional theory (DFT) calculations and the periodic supercell approach, the oxygen reactivity at the interface of pristine and B-doped graphene with both crystalline Cu (111) [1,2] and anatase TiO₂ (101) surfaces [3]. In this talk we will present an overview of our results. We will show that, to properly describe interface distances, adhesion energies, electronic properties and charge transfer effects, the use of Van der Waals corrected methods is mandatory. In the case of TiO₂, some portion of exact exchange, as in the hybrid functional approaches, is also required, to avoid spurious effects deriving from an underestimated band gap value for the semiconducting oxide. The presence of oxygen at the interface is found to enhance the adhesion energy of pure and doped graphene with both substrates. The role of the dopant is to increase the interaction with the oxygen atoms. All these observations indicate a positive effect of oxygen confinement at a graphene/substrate interface in terms of improved reactivity, interfacial charge transfer and electronic states hybridization.

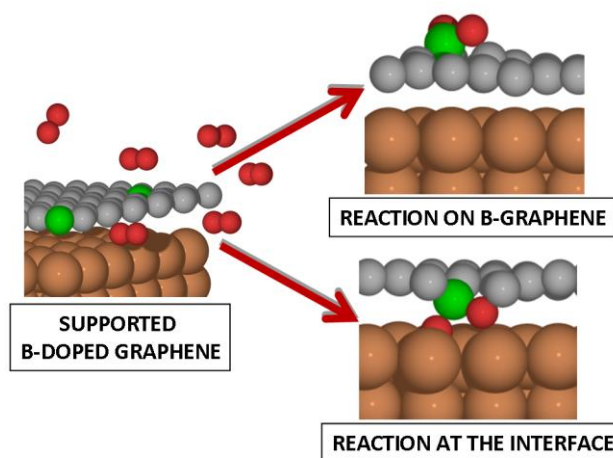


Figure 1: Schematic representation of oxygen reactivity at the doped graphene/support interface.

References:

- [1] L. Ferrighi, M.I. Trioni, C. Di Valentin *J. Phys. Chem. C* **119**, 6056-6064 (2015).
- [2] L. Ferrighi, C. Di Valentin *Surf. Sci.* **634**, 68-75 (2015).
- [3] L. Ferrighi, G. Fazio, C. Di Valentin, under review.

In situ surface structure determination during catalytic reactions using high-energy surface X-ray diffraction

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Surface X-ray diffraction (SXRD) is one of few methods available for surface structure determination under ambient conditions. Using conventional SXRD, however, exploring 2D maps from a substantial part of reciprocal space is extremely time-consuming, and mapping of the 3D reciprocal space with high resolution is currently impossible even with synchrotron radiation. As a result, the probed surface structure has to be known qualitatively from other measurements, and an unexpected structure may easily be left unnoticed, especially under harsh conditions.

In this contribution I will demonstrate how the use of high-energy X-rays (85 keV) in combination with a large 2D detector accelerates the data collection by several orders of magnitude and enables full surface-structure determination by 3D mapping of reciprocal space on a time scale suitable for in situ studies [1]. In addition, the small diffraction angles, resulting from the high photon energy, and the large detector result in data that are easily presented in a more intuitive way, since each detector image contains the projection of a full plane in reciprocal space and straight lines in reciprocal space correspond to straight lines on the detector.

We have used this method to analyse the structure of ultra-thin surface oxides formed on Rh(111), Pd(100) and Cu(111). Especially, we have followed how the presence and nature of these oxide varies with the catalytic activity towards CO oxidation and CO₂ reduction.

References:

- [1] J. Gustafson, M. Shipilin, C. Zhang, A. Stierle, U. Hejral, U. Ruett, O. Gutowski, P.-A. Carlsson, M. Skoglundh, and E. Lundgren, *Science* **343**, 758 (2014).

Revisiting old and exploring new surface science with curved crystals: Pt and TiO₂

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Stepped surfaces have frequently demonstrated their enormous potential from both scientific and technological points of view. They exhibit distinct chemical and physical properties due to their high density of atomic steps, being also useful as nanoscale templates to control the growth of low dimensional structures, such as nanostripes. However, it is not a-priori clear whether a stepped surface, e.g., improves or worsens the growth of a specific material, or promotes or disturbs a given surface chemical reaction. One key parameter is the step density $1/d$, which may be critical, e.g., to enhance gas/surface heterogeneous catalysis. Using surfaces with curved shape one can smoothly vary the surface crystal orientation, i.e., the step-density $1/d$ on a single sample, allowing a rational assessment of the influence of steps on physical-chemical processes.

Very recently, we have fabricated and utilized curved Pt and TiO₂ surfaces (Figure). In all cases our results demonstrate the enormous potential of the curved surface approach, not only to transparently settle largely-debated surface chemistry problems, but also to reveal new, subtle $1/d$ -properties of stepped surfaces. Such properties nicely arise when the curved surface is scanned with spectroscopic and microscopic probes. In particular, Scanning Tunnelling Microscopy (STM), and high-resolution X-ray Photoemission Spectroscopy (XPS), the latter using the standard 100 μ m spot size beam provided in synchrotron facilities.

In curved rutile TiO₂(110) we study the interplay between the two chemically-active sites, namely steps and oxygen vacancies at (110) terraces, and analyse the contribution of steps to the doping charge of the bulk TiO₂ crystal. We reveal the existence of a magic $1/d$ density where oxygen bridge vacancies vanish. In curved Pt(111), we study the equilibrium shape of stepped surfaces and revisit the chemisorption of CO in the presence of surface steps. We demonstrate, for the first time, the universal transition from elastic to entropic step interactions, triggered by the increasing compressive strain at the stepped surface. For the CO chemisorption, we reveal a subtle C 1s core-level shift, suggesting a change in compressive strain as a function of $1/d$.

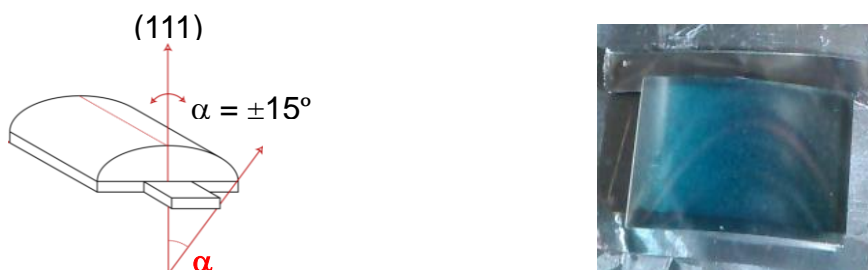


Figure 1: (a) Sketch description of the Pt(111) curved crystal. (b) Photograph of the curved TiO₂(110) rutile surface.

Nanoscale Origin of Mesoscale Roughening in Ruthenium Oxidation by O₂

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Low-energy electron microscopy (LEEM) is a technique that allows for in situ monitoring of surface processes in reactive environments at nanometer length scales and at video rates [1]. While the qualitative interpretation of the image sequences for simple enough systems appears quite straightforward, understanding the detailed structure in multicomponent systems such as, e.g., those found in oxide heteroepitaxy and inverse model catalysts, is much more intricate. A possible solution to this enigma is the analysis of the dependence of the specular electron reflectivity on the kinetic energy of the incident electrons, also known as the (00)-beam I(V) curve in low-energy electron diffraction (LEED). This I(V) curve contains detailed information on the geometric and electronic structure of the probed sample surface. In low-energy electron microscopy experiments, which typically are performed at fields of view in the range of a few microns or more in diameter, this dependence can be used for tying together mesoscale morphological observations and dynamics with nanoscale atomic and electronic structure [2]. Furthermore, μ LEED experiments can be conducted using electron beam diameters down to a few hundred nanometers, providing local insights into surface periodicity and morphology.

In this contribution, we will use the capabilities of I(V)-LEEM and μ LEED for real-time studies of the oxidation of the Ru(0001) surface by exposure to molecular oxygen at elevated temperatures, allowing for characterizing and distinguishing different oxide orientations that concurrently evolve with increasing dose [3,4]. Interestingly, the RuO₂(100) orientation is shown to nucleate first whereas the well-known majority RuO₂(110) phase only develops at a later stage, concomitant with the growth of the (101) orientation. We will explain how this counter-intuitive growth scenario can be explained and how this complex oxidation behavior gives rise to roughening on the mesoscale.

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Automated surface structure determination with DFT

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Using density functional theory, we conduct unbiased searches for the optimum structures of stepped TiO₂(110) surfaces and Au nano-particles on flat rutile TiO₂(110). The searches employ our implementation of a genetic algorithm for structural optimization [1]. For the stepped TiO₂(110) surfaces, extra TiO₂ units are found to decorate the step edges with the Ti atoms at non-bulk positions. These structural motifs would have been difficult to identify without the automated structural search method [2]. The implications of the new step structures for adsorbates and surface reactions are discussed [3,4]. On flat TiO₂(110) the DFT calculations point to the presence of oxygen at the entire interfacial area between supported gold nano-particles and the oxide surface [5]. The interfacial oxygen atoms cover the 5-fold Ti atoms in the troughs of the (110) surface. Again, it will be stressed that the identification of this structural element is non-trivial and strongly rely on the use of the automated structural search method. A 24 atom Au cluster is optimized with the same methods and its activity towards the CO₂ formation from CO and oxygen is studied and comparisons are made for various edge and corner sites showing a large variation in the local chemical activity[6].

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Surface Structures of Ultrathin Ti₂O₃ Films on Au(111)

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Titanium oxides are materials used in photocatalysis [1] and gas sensing [2]. Most of the studies are based on the two common TiO₂ polymorphous – rutile and anatase. However, new titanium oxide structures can be created in ultrathin film forms that are very different from the bulk crystal terminations. There is increasing interest in this field because these novel structures may be associated with enhanced properties.

We have carried out growth of TiO_x ultrathin films on (22 × √3)-reconstructed Au(111) substrates through Ti deposition and post-deposition oxidation and annealing. In the growth of the thin films three different structures were observed: a (2 × 2)-reconstructed Ti₂O₃ structure resembling a honeycomb pattern, a TiO pinwheel shape and triangular shaped TiO_x islands [3,4]. The (2 × 2) honeycomb structure has two crystallographically unique domain boundaries (DBs) along the <1-10> directions, and also two unique DBs along the <11-2> directions. Along the <11-2> directions the preferred boundary structure is to have alternating rings of 4 and 8 Ti atoms. Along the <1-10> directions there are two commonly observed DBs with either double 5-fold and single 8-fold rings or with alternating 5-fold and 7-fold rings. Scanning tunnelling microscopy (STM) images of these three DBs are shown in figure 1. Density functional theory (DFT) calculations were used to model the DB structures and to calculate their formation energies. Two DBs that are crystallographically unique, but are not observed by STM over long repeat periods, were also modelled.

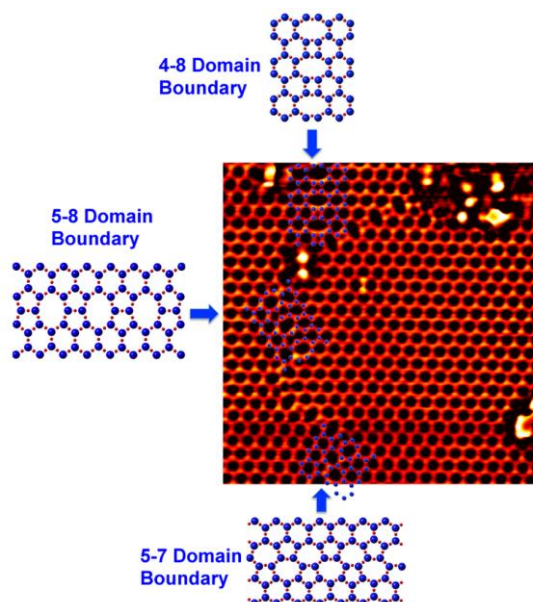


Figure 1: STM image of Ti₂O₃ honeycomb thin films with 4-8, 5-8 & 5-7 DBs (image size: 14 × 14 nm², V_s = 0.9 V, I_t = 0.22 nA). Ti atoms are drawn as big blue balls; O atoms are small red balls.

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The influence of Mg of the surface properties in rutile TiO₂(011)

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Titanium dioxide is a metal oxide with many relevant technological properties for photocatalysis, chemical reactivity, electrical conductivity and solar energy harvesting. TiO₂ is an inert insulator in stoichiometric form and it can be easily reduced into an n-type semiconductor TiO_{2-x} with the transformation of Ti⁴⁺ to Ti³⁺ ions. This reduction is also characterized by the excess electrons populating localized Ti3d states in the band gap [1]. These electrons can be well characterized by the presence of a defect state at about 0.8 eV below the Fermi level [2]. Moreover, in the case of very low defect content, Ti3d states can be exalted through resonant valence-band photoemission process where, at resonance, the direct photoemission of a valence-band electron interferes with the two-step autoionization process leading to the same final state. It has been measured the angular distribution and the corresponding PhotoElectron Diffraction (PED) pattern of the defect state in resonant conditions for the rutile TiO₂(110) surface and mapped its distribution in the case of a non-stoichiometric surface [3] and after deposition of Na on a stoichiometric surface [4]. The main finding was the demonstration that charge distribution of the band gap state is essentially an intrinsic property of the TiO₂ (110) surface, because largely independent of the way excess electrons are created. Within this framework we studied another rutile surface – the (011) – in the presence of Mg. Mg is a common contaminant of TiO₂ and, by thermal annealing of the sample, it is possible to make it segregate from the bulk of the sample up to the surface. Both core level and valence band photoemission experiments were performed and the spectra show a decrease of the defect state linked to Mg presence. PED patterns were also recorded in order to study the localization of magnesium in the TiO₂ surface layers. The experimental data set allows to exclude the formation of metallic Mg clusters on the surface and, rather, to point to the substitution of Mg into the Ti lattice sites. The decrease of the defect state intensity in the band gap observed in the presence of Mg is due to the formation of MgO which takes the role of “metal oxide dopant” for the TiO₂, since doping with a metal oxide (i.e. ionic doping) does not induce electron excess.

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The oxide-oxide interface in reducible oxides: a new paradigm in nanocatalysis

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Surface science studies are clearly delineating a consistent paradigm pointing to the use of interfaces as an effective tool for stabilizing highly active chemical species. So far the most commonly used approach consists of supporting oxides on metals since it is possible to take advantage of the electronic interactions at the interface that can increase the adhesion of the oxide or modify its electronic properties. However, an alternative path, thus far less explored, is the formation of oxide-on-oxide interfaces [1].

Recently, we studied the growth of vanadia [2,3] and ceria [4] thin films on TiO₂(110) and studied their structural and chemical properties. In the case of vanadia the combination of STM photoelectron diffraction and DFT calculations has allowed identifying the formation in the submonolayer regime (<0.3 ML) of peculiar V₄O₆ nanoclusters, which hold vanadyl groups, even if vanadium oxidation state is formally +3 [2]. Moreover, our theoretical investigation indicates that on the surface of titania, vanadia mononuclear species, with oxidation states ranging from +2 to +4, can be strongly stabilized by aggregation into tetramers that are characterized by a charge transfer to the titania substrate. The combination of HREELS, STM, and NEXAFS suggests that for higher coverage vanadia maintains V³⁺ oxidation states, but modifies its growth morphology from [001] oriented nanostripes (0.5-1 ML) to compact nanoislands (2-5 ML) [3]. Thermal programmed desorption experiments demonstrated that each nanostructure despite presenting vanadium atoms in the same chemical state, exhibits a quite unique reactivity towards ethanol oxidation [3].

More complex oxide nanophases can be obtained as a consequence of ceria deposition on TiO₂(110) [4]. At low coverage dumbbell nanostructures constituted by reconstructed titania and ceria clusters are formed whereas at higher coverage long range ordered ceria films with c(4x4) and p(2x6) periodicity are formed. Interestingly, the spectroscopic investigations of these films indicates that ceria is exclusively present in 3+ oxidation states thanks to the electronic interaction between Ce 4f and substrate O 2p bands. The special electronic properties of these films have a direct counterpart in the chemical activity, which has been investigated by temperature programmed desorption, using methanol as a probe molecule. The experimental results indicate an exceptional activity of the ceria-titania interface in the selective dehydration of methanol to formaldehyde at unprecedented low temperature (330 K) [4].

Our results therefore help to substantiate a new paradigm in nanocatalysis, which identifies the common origin of the high chemical activity of these systems in the peculiar properties of interfaces that can stabilize unusual structures or highly active chemical species either by electronic hybridization (CeO_x/TiO₂) or by charge transfer (VO_x/TiO₂). Interestingly, the concepts developed by model studies in UHV conditions have been exploited for the preparation of titania@ceria core@shell nanoparticles, which can be used as catalysts with biomimetic activity [5].

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Finite-Temperature Effects on Structure and Energetics: Organic Adsorbates from a First-Principles Perspective

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An often imposed assumption in vacuum surface science is that equilibrium properties of molecular adsorbates on metal surfaces are largely unaltered by finite temperature effects. This talk revisits this assumption for large organic adsorbates in the context of surface functionalization and hybrid organic--inorganic interfaces. Employing Density-Functional Theory including the account of many-body dispersion effects we assess the accuracy of geometries and adsorption energies for a variety of systems in comparison to X-ray standing wave and Temperature Programmed Desorption (TPD) measurements, both experiments usually performed at medium to high temperatures. Specifically for functional and flexible adsorbates the above assumptions break down as here shown for the molecular switch azobenzene adsorbed on an Ag(111) surface. Only by explicit account of anharmonic effects and vibrational mode coupling using *ab-initio* molecular dynamics are we able to correctly recover the experimental adsorption geometry and temperature. This not only raises questions concerning the reliability of typical approximations in simulation, but also has consequences for the typical TPD analysis in the framework of the Polanyi-Wigner equation.

“Hot” adatoms hopping: Phononic dissipation & equilibration dynamics from first-principles

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Exothermic surface chemical reactions may easily release several electron volts of energy. This challenges first-principles based dynamical simulations to account for adequate energy dissipation channels. Focusing on phononic dissipation, a novel embedding scheme for metallic substrates allows for energy to be dissipated out of a quantum-mechanically described reaction zone and into a computationally undemanding, yet reliably described, extended bath [1]. In the application to oxygen dissociation over Pd(100) this predicts “hot” dissociation fragments traveling ballistically over several lattice constants as a consequence of non-immediate energy transfer to the metal surface. This raises fundamental questions when considering the short-range transient mobility measured experimentally for the similarly exothermic O₂/Pd(111) reaction [2]. Here, we elucidate phononic dissipation within the (111) as compared to the (100) surface and explain the small net displacement by revealing randomized trajectories of hyperthermal hops between neighboring hollow sites due to scattering by the strongly corrugated chemisorption potential. We therefore invalidate the simplistic physical picture implying a minimal number of hops for small adatom separations and anticipate further paradigm shifts required to accommodate such “hot chemistry”, for example, in our current understanding of heterogeneous catalysis.

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Dynamics of Repulsion-Induced Surface-Migration by Ballistics and Bounce

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The motion of adsorbate molecules across surfaces is fundamental to various fields including self-assembly, material growth, and heterogeneous catalysis. Scanning Tunneling Microscopy (STM) has shown electron-induced long-range surface-migration of ethylene, benzene and related molecules, moving across distances averaging ~ 50 Å on Si(100) [1-2]. This motion was ascribed to the effect of a sudden repulsion operating between the adsorbate and the surface. However, dynamical studies have not previously been made.

Here we postulate for electron-excited ethylene at Si(100) that the energy of the electron (~ 2.9 eV) has been converted to repulsion. This we simulate by compressing the chemisorbed adsorbate symmetrically or asymmetrically by 0.3-0.4 Å against the surface, a seven-layer slab of Si₁₁₂H₃₂ (terminated below with H). The molecular dynamics following the release of this repulsion constitutes the subject of the present study.

The repulsion excites bending of CH₂ in the ethylene which, in subsequent V-T (vibration-to-translation) energy-transfer, gives sufficient velocity of the ethylene centre-of-mass away from the surface and along it to break the two C-Si bonds. The resultant motion is that of a physisorbed ethylene arcing upwards in a ballistic trajectory to peak heights in the range of 5-7 Å, out of range of the surface roughness, which has fallen by orders of magnitude as the height is increased. Ballistics carry the molecule tens of Angstroms along the direction perpendicular to the Si(100) dimer-rows - the direction observed experimentally. Such 'cannon-ball' behaviour has been postulated by previous authors; here we compute its molecular dynamics, under the influence of repulsion and the van der Waals attraction that operates on a neutral species.

Significantly, these dynamics indicate that ballistic flight alone is insufficient to explain the observation of directed migration over distances as large as 200 Å [1-2]. Long-range travel is found to be due to a succession of ballistic events linked by bounces at the silicon surface.

We predict comparable behaviour in other cases where an atom or molecule recoils at an angle from the surface. Here we use an "impulsive two-state" model to compute the long-range recoil of atomic chlorine in an ab initio field of force, following electron-induced dissociation of chlorophenyl on Cu(110).

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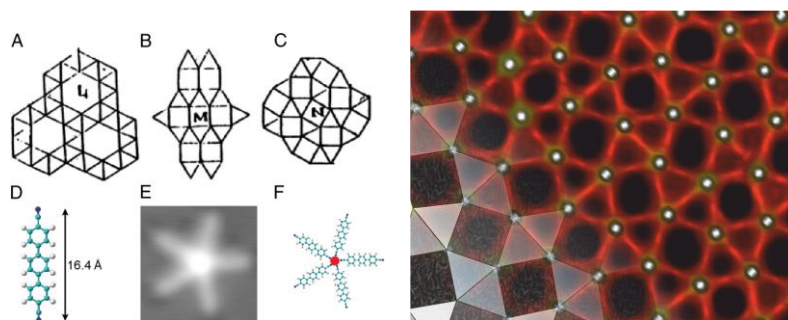
Pathways to complex interfacial networks and 2D tessellations

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A major objective in modern surface and nanoscale science is the study of complex interfaces and the development of protocols for their control, both in the static and dynamic regime. Fascinating examples regarding self-assembled networks on solid surfaces include hierarchical assemblies, pentagon tilings, or glassy 2D architectures. Moreover, intricate chirality phenomena and glassy networks were recognized, and quasicrystalline order was observed in epitaxial and soft-matter self-assembled systems or polymers. Herein we report advances towards surface-confined complex networks using metal-directed assembly on surfaces. This approach constitutes a versatile route to design low-dimensional nanoarchitectures, frequently affording a favorable balance between robustness and spatial regularity. We convey the general strategy, give various examples and highlight networks and tessellations comprising (i) rare-earth metal centers and (ii) flexible molecular units, where intriguing ordering phenomena unfold.

Following the first approach, by taking advantage of lanthanide centers for the engineering of surface coordination nanostructures and layers, we achieved a 2-D pattern known as the "semiregular snub square tiling", representing a molecular-level demonstration of one of the canonical tessellation patterns Johannes Kepler described more than 400 years ago (cf. Fig. below). This becomes possible by fivefold Ce- (or Gd)-ligand CN-coordination motifs, which are planar and flexible, such that vertices connecting simultaneously trigonal and square polygons can be expressed. With the right concentration and stoichiometric ratio of rare-earth metal centers to ligands fully reticulated layers are expressed providing large domains of the prevailing snub square tiling. In addition, using Eu centers on Au(111), a random square-triangle tessellation with dodecagonal rotational symmetry evolves, associated with 2D random tiling quasicrystallinity. [1]



Left panel: (A–C) Five-vertex Archimedean tilings of the plane as sketched by Johannes Kepler in *Harmonices Mundi*. (A) Snub hexagonal tiling, (B) elongated triangular tiling, and (C) snub square tiling. (D–F) Fivefold coordination node of cerium and carbonitrile linkers on Ag(111). (D) Para-terphenyl-dicarbonitrile; C (H, N) atoms in green (white, blue). (E and F) STM image and model of isolated pentameric Ce–carbonitrile coordination unit. Central panel: Five-vertex Archimedean surface tessellation by fully reticulated rare-earth-organic networks. Right panel: STM overview data of quasicrystalline network following Eu-directed assembly of para-quaterphenyl-dicarbonitrile on Au(111) at a $\sim 5:1$ stoichiometric ratio.

Regarding (ii) we notably investigated a 1,3,5-tris(pyridin-4-ylethynyl)benzene linker with three pyridyl groups connected to a central aryl ring through ethynyl moieties. The molecule is specifically equipped with pyridyl functional groups to steer a simultaneous expression of lateral pyridyl–pyridyl interactions and Cu–pyridyl coordination bonds. Carefully developed assembly protocols yield a new class of porous open assemblies, the formation of which is driven by multiple

interactions. We notably identified superlattice formations interpreted in terms of 2D short-range disordered crystalline networks, i.e., sheet materials that displays a discrete diffraction diagram and present any of the following ordering characteristics: (1) the constituents are positioned following a crystalline lattice, but at the same time disordered with respect to their orientational or distortional degrees of freedom, or (2) the intermolecular links span a crystalline lattice, but the molecular building blocks present distortional or orientational short-range disorder [2].

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What can we learn from high-resolution AFM/STM images: mapping molecular electrostatic potential

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High-resolution AFM images of single molecules [1] allows bond-order discrimination [2] or identification of a priory unknown molecules [3]. The origin of the high-resolution AFM contrast is caused by bending of functionalized probe due to tip-sample interaction [2,4]. The bending is mainly driven by van der Waals (vdW) and Pauli repulsion. Recently, we noticed that the electrostatic interaction acting between the probe and the inspected molecule could significantly modify the submolecular contrast [5]. Here we present a new experimental protocol, which provides straightforward way to resolve the local electrostatic field of a single molecule by means of AFM with functionalized tips with unprecedented resolution. We show that difference between two high-resolution images acquired at different conditions contains information about the local electrostatic field. Application of elastic deformation technique provides deformation vector field, which can be converted into the local electrostatic field.

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Taking a stand: aromatic molecules in vertical adsorption geometries

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In most cases, large π -conjugated organic semiconductor molecules adsorb with their molecular planes parallel to the metal surface on which they are deposited. This behavior is governed both by the van der Waals attraction and the chemical interaction of the π -system with the metal. However, under certain circumstances this general behaviour can be altered, even on metals. Three examples will be presented, ranging from a coverage-driven chemical dissociation reaction the products of which adsorb upright [1], via the skilful use of kinetic constraints to obtain the autocatalytic growth of a vertical phase [2], to the purposeful manipulation of molecules into an upright geometry [3]. Mechanisms and applications will be discussed.

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Anhydride and Polyanhydride Formation By Phthalic Acid on Ag(100)

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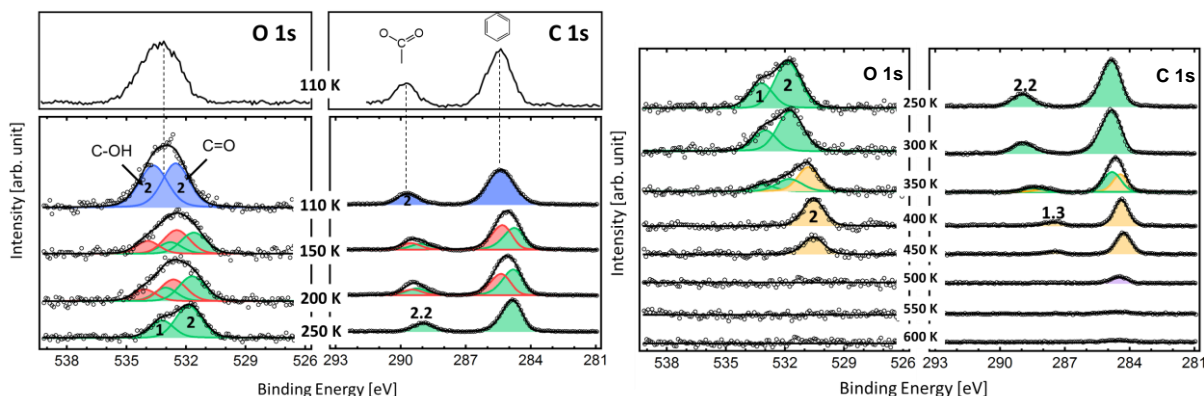


Figure 1: O 1s and C 1s photoemission spectra of 0.5 ML phthalic acid adsorbed on Ag(100) at 100 K and annealed to the indicated temperatures.

Large organic molecules with carboxylic acid groups have been used extensively in scanning probe studies, mostly at room temperature, to form large, ordered two-dimensional networks on metal surfaces. The driving force for the formation of the large, ordered structures is often assumed to be hydrogen bonding between the carboxylic acid groups. However, by studying the adsorption of phthalic acid on Ag(100) with synchrotron photoemission at Elettra combined with temperature-programmed desorption studies in our home lab, we can show that on Ag(100) the acid groups react to form anhydrides already at 150 K and that the stable species on the surface at room temperature must be a polyanhydride and not a carboxylic acid. Above 400 K, a stepwise decomposition of the polyanhydride occurs until, at 700 K, only carbon remains at the surface. The project has been supported by the DFG through FOR 1878 (funCOS).

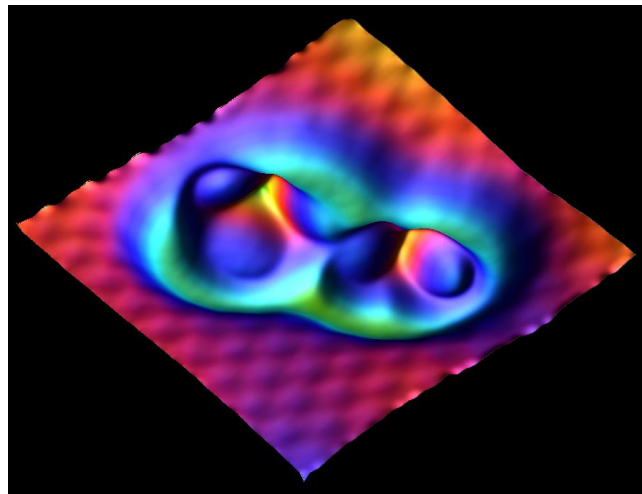
Hot spots in atomic force microscopy

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Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) image surfaces with atomic resolution and enable local spectroscopy of current versus voltage, forces and dissipation. The qPlus force sensor [1] combines STM and AFM capability, enabling highly precise imaging and spectroscopy functions and measuring the forces that act during atomic manipulation [2]. While STM had better spatial resolution than AFM in the past, the situation is reversed now with modern AFM [3]. Angular dependencies of chemical bonding forces have been observed before for Si tips interacting with Si surfaces [4], W tips interacting with graphite [5] and similarities exist between metal tips interacting with CO molecules on Cu and Si adatoms [6]. In the latter two cases, light atoms such as carbon or oxygen interacted with much heavier and much larger metal atoms. Gross et al. established that CO is an excellent probe for organic molecules. For example, pentacene can be imaged at excellent resolution with CO terminated tips [7], although the softness of CO on tips can lead to image distortions [8,9]. Tips made of permanent magnets such as CoSm allow to resolve the spin order in the antiferromagnetic insulator nickel oxide [10]. The stiff cantilever/small amplitude technique used here also allows true atomic resolution in ambient conditions [11], and small iron clusters on Cu (111) are resolved by force microscopy [12]. In summary, we see three hot spots in modern AFM development: excelling in spatial resolution, force resolution and overcoming environmental operational limits.



AFM image of a Fe trimer next to a Fe dimer on Cu(111) [12].

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Metal growth on graphene: morphology, intercalation and magnetization

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Graphene based electronic and spintronic devices require understanding of the growth of metals on graphene. Several metals (Gd, Dy, Eu, Fe, Pb) were studied with STM and DFT. The grown morphology (island density and domain size distributions) was used to extract the metal diffusion and adsorption barriers. For practically all metals the grown mode is 3-d as a result of the low ratio of the metal adsorption energy on graphene to the metal cohesive energy[1]. It is essential to find ways to modify the growth to layer-by-layer for high quality metal contacts in graphene devices and for using graphene as spin filter. These experimental results are fully supported with DFT calculations.

The growth of Fe on graphene is unusual because the nucleated island increases continuously with deposited amount which indicates the presence of long range repulsive interactions. [2]. An advantage is the tunability of the island density which can be useful for magnetic storage applications. Dy was found to grow fcc(111) instead of hcp(0001) islands expected from its bulk structure. This is seen from the triangular island shape and the ABCABC (instead of ABABAB) stacking sequence of islands nucleating on successive layers[3].

Ex situ SMOKE magnetization measurements on the Fe islands show a transition from superparamagnetic to ferromagnetic islands with coverage. XMCD measurements on the Dy islands show that the islands are paramagnetic.

Initial experiments on graphene partially intercalated with Dy show that nucleation is preferred on the intercalated areas, which can be used for patterning metal films grown on graphene.

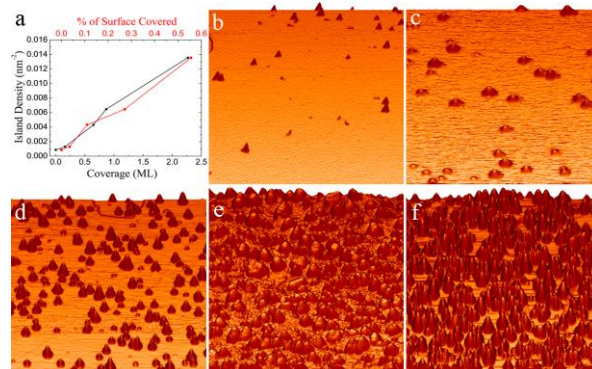


Figure 1: 200x200nm² Fe nucleation on graphene shows increasing Island density with Fe deposited amount

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Microspectroscopy and micro-diffraction analysis of transient, nanoscale cerium oxide phases during reduction by molecular hydrogen

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Ceria is a highly versatile oxide and used in many catalytic applications today; however, its structure-function relation and true active nature in chemical redox reactions are still not well understood. An important example is the interaction of ceria with molecular hydrogen, which is an integral part of the hydrogenation process that produces methanol from CO₂ ($\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$). Here, employing a powerful combination of electron spectromicroscopy with synchrotron radiation, low-energy electron microscopy, and micro-illumination diffraction analysis, we follow *in situ* the complex structural transformations of a well-defined ceria/Ru(0001) model catalyst system when exposed to a reactive H₂ environment [1]. Specifically, by modeling the time-dependent, experimental diffraction profiles acquired during the reduction process (see left figure) we demonstrate that the transition from CeO₂ to crystalline Ce₂O₃ occurs through a mixture of transient, ordered cerium oxide phases whose average size is on the order of just a few nanometers. Furthermore, these crystalline surface phases are shown to exhibit characteristic intensity-voltage curves, which allow their spatial distribution directly to be imaged in real space (right figure).

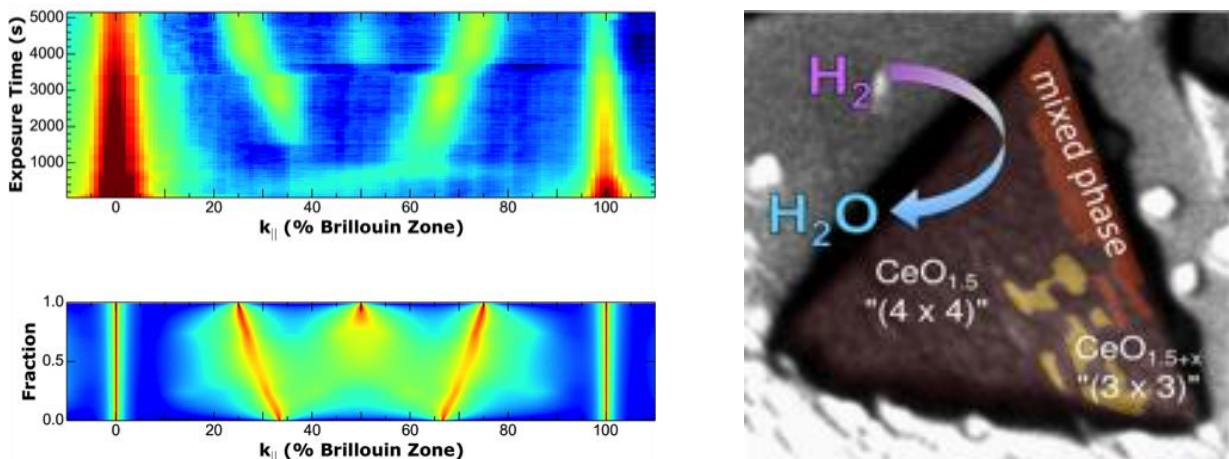


Figure 1: (left) Evolution of *in situ* LEED profiles (top panel) from CeO₂(111) to Ce₂O₃(111) and comparison to simulations (lower panel). (right) LEEM image of a reduced cerium oxide island with oxidation state contrast.

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Structures, Interactions and Dynamics of Alkylimidazolium Ionic Liquids at the solid–liquid interface

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While known for about a century, ionic liquids – commonly defined as salts with a melting point around or below room temperature – have become a staple in electrochemistry over the course of the last ten years. Their unique properties, including a large electrochemical window, makes these substances particularly interesting for the development of novel applications such as high-capacity batteries, supercapacitors or fuel cells [1][2]. While downsizing technology, in an attempt to build smaller, yet more powerful devices, interface effects become more and more dominant in the system. Therefore, our studies focus on the structural details, liquid–substrate interactions and dynamics of common protic ionic liquids (1-alkyl-3-methylimidazolium–bis(trifluoromethylsulfonyl)imide) at the solid–liquid interface. Employing a complementary approach of X-ray reflectivity and molecular dynamics simulations, we are able to present reliable information on layering phenomena (a) – where an alternating sequence of cation- and anion-enriched monolayers was observed –, intercalating lateral ion structures at the interface (b), preferred orientation of ions near the substrate (c) – providing that hydrogen bonding is dominant for hydroxylated substrates – and interface dynamics in comparison to the bulk liquid [3].

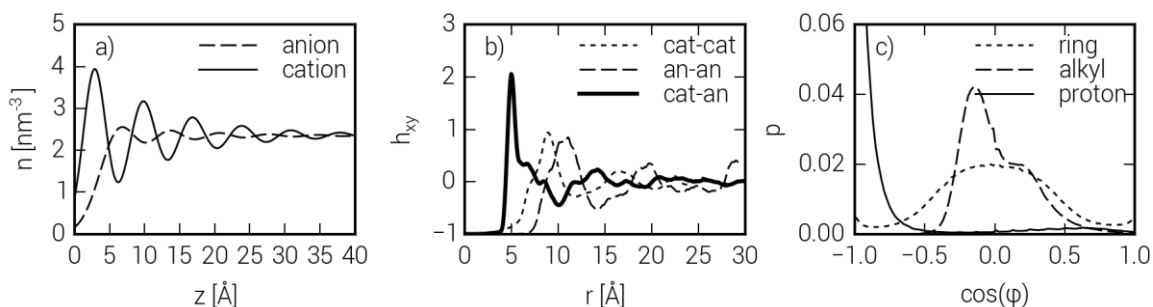


Figure: Interface-normal number density of ions inferred from experiment (a), lateral density-density correlation of cations and anions in the first layer (b) and orientational distribution of the cations' alkyl chains, imidazolium ring normals, and acidic ring protons in respect to the interface normal unit vector.

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Exploring 2D materials via high-resolution electron and scanned probe microscopies

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The microscopic characterization of two-dimensional materials, and low-dimensional matter in general, poses unique challenges but also opens unique new avenues that are different from those of 3-D bulk structures or the surfaces of 3D crystals. In this talk, I will discuss some of these aspects in connection with high-resolution electron microscopic studies as well as scanning probe investigations. The study of nano-carbons and other low-atomic number materials remains a particular challenge for high resolution transmission electron microscopy (HRTEM) or scanning transmission electron microscopy (STEM) owing to their intrinsically low contrast and high susceptibility to radiation damage. However, the recent developments in aberration-corrected electron optics open a route to atomically resolved studies of these materials at reduced electron energies, below the knock-on threshold of carbon atoms in graphene [1]. I will present insights to this class of materials from electron microscopic studies with single-light-atom precision. At the same time, the electron microscope can be used to structure and modify graphene with highest resolution and with a direct feedback [2]. We analyzed the mechanisms behind beam-driven structural changes and demonstrate how a controlled modification, beyond the ejection of atoms, can be achieved. As a complementary tool of atomic-level analysis, scanning probe microscopy and in particular scanning tunneling microscopy (STM) has been extensively used for studying graphene and related materials. While most studies focus on “supported” graphene and other 2D materials, I will discuss STM studies of freely suspended graphene membranes. I will show initial results from a dual-probe STM setup where a free-standing graphene membrane is probed simultaneously from opposing sides [3], so that at the closest point, the two probes are separated only by the thickness of the membrane. In this way we could measure the deformations induced by one STM probe on a free-standing membrane with an independent second probe, reveal different regimes of stability of few-layer graphene, and show how the STM probes can be used as tools to shape the membrane in a controlled manner.

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A joint DFT and XSW study in to the “surface *trans*-effect”: If it looks like a duck, swims like a duck and quacks like a duck, is it actually a *trans*-effect?

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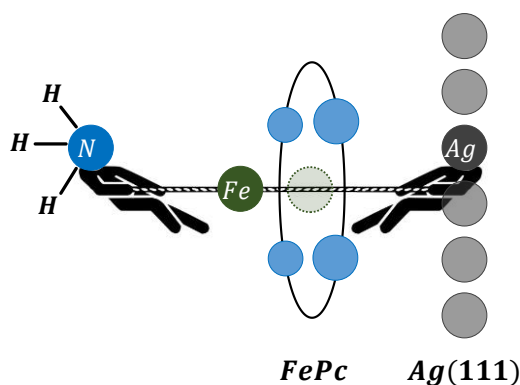
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The interaction of ligands with metal-organic complexes immobilised onto a metal surface has been cited as a potential system for a wide variety of applications [1], however the physical understanding at this interface is still largely lacking. Observations of a larger than expected electronic effect from the ligations of relatively simple molecules [2] has led to the suggestion of a so called “surface *trans*-effect” (STE) [3]. The *trans*-effect is a well-known effect in coordination chemistry, in which the coordination of a “strong *trans*-ligand” will weaken the interaction between the ligand *trans* to it and the central metal atom. The STE, instead, has the “*trans*-ligand” weakening the interaction between the central metal atom and the underlying substrate. It is this weakened interaction between the metal-organic complex and the substrate that results in the larger than expected electronic effects observed by Flechtner et al. [2]. The theoretical calculations of Hieringer et al. [3], supporting this assignment, also predicted a significant structural displacement.

Here we present a joint experimental and theoretical study into this effect, focusing on quantifying this displacement of a metal-organic adsorbed on a metal surface. Specifically the displacement of iron phthalocyanine on Ag(111) due to the ligation of ammonia and water was studied by normal incidence X-ray standing waves. Excellent quantitative agreement was found with density functional theory calculations after the inclusion of dispersion corrections; the central Fe ion was found to be “pulled” out of the surface by $0.19 \pm 0.04 \text{ \AA}$ by ammonia and $0.07 \pm 0.04 \text{ \AA}$ by water.



Therefore several phenomena have been observed that strongly suggest a ground state *trans*-effect, and some weak evidence that suggests a kinetic *trans*-effect [4], is occurring with the metal surface acting as such a *trans*-ligand begging the question: is this actually a *trans*-effect, or does it merely look like one?

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Dynamics of copper-phthalocyanine in the molecular bridge position

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Spatially resolved current-time scanning tunneling spectroscopy combined with current-distance spectroscopy is used to characterize the dynamic behavior of Cu-phthalocyanine (CuPc) molecules adsorbed on a Au-modified Ge(001) surface. CuPc molecules adsorb onto the Au-nanowires in a “molecular bridge” position where the molecule bridges between two adjacent nanowires. Three types of benzopyrrole (lobe) configurations are found, a bright lobe, a dim lobe and a fuzzy lobe configuration. The dim and fuzzy lobes exhibit well defined switching between two well defined levels where the bright lobe shows a broad oscillation band induced by electrons that are directly injected into the LUMO+1 orbital of the CuPc molecule. By precisely adjusting the tip-molecule distance, the switching frequency of the lobes can be accurately tuned.

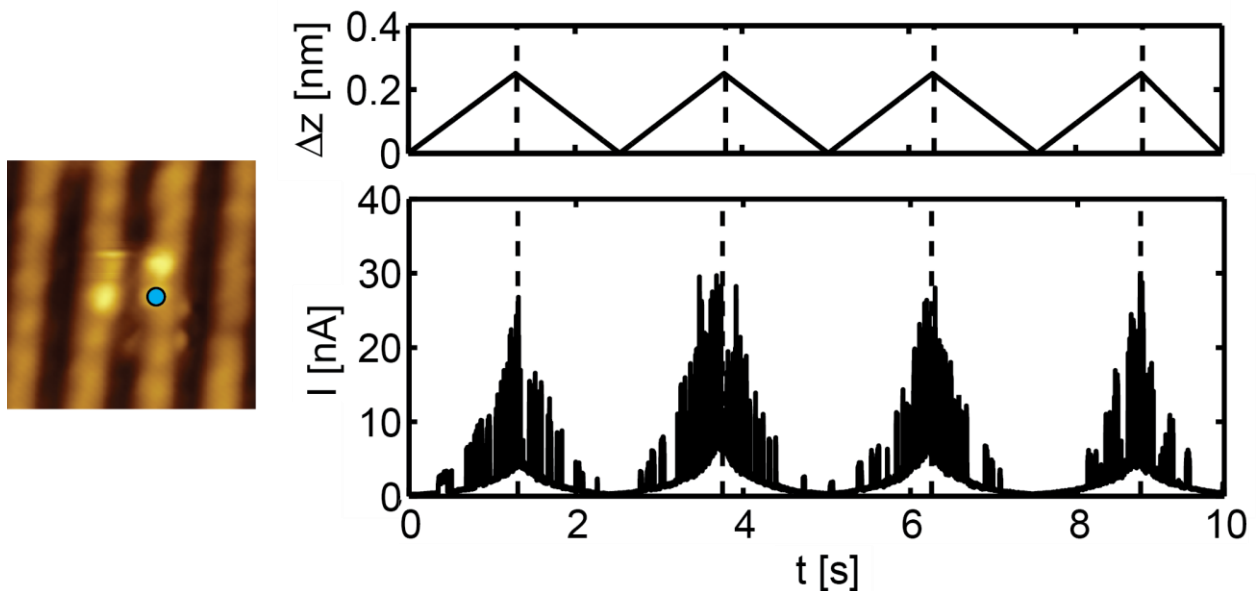


Figure 1: The current response of the dim lobe of a CuPc molecule in the four lobe bridge configuration (bottom image) when the tunnel gap distance is altered as in the top image.

Ordered growth of vanadyl phthalocyanine (VOPc) on an iron phthalocyanine (FePc) monolayer: local V=O-Fe bonding?

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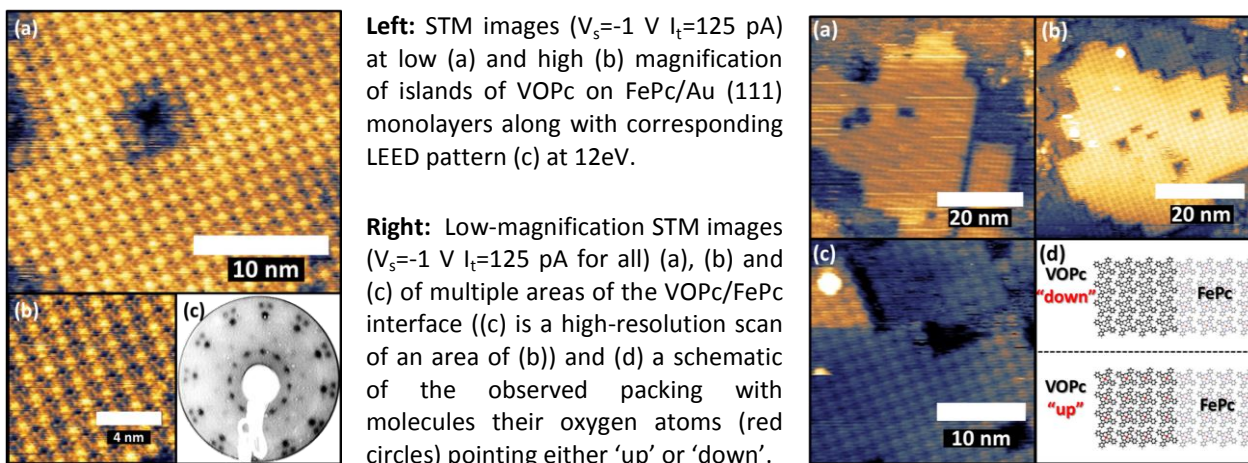
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The growth and characterisation of a non-planar phthalocyanine (vanadyl phthalocyanine, VOPc) on a complete monolayer of a planar phthalocyanine (iron (II) phthalocyanine, FePc) on an Au (111) surface, has been investigated using UHV scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED). The square surface mesh of the initial FePc monolayer (consistent with the square symmetry of the molecule) has been determined through the combination of STM images and simulations of the LEED patterns. These show the overlayer to be incommensurate, not commensurate as previously reported, but azimuthally aligned such as to have only three rotational domains. Previous STM images of VOPc grown directly on metal surfaces have been variously interpreted as indicating that the V=O points out from the surface or V=O points down to the surface. These different assignments have relied on whether the centre of the molecule images in STM as a protrusion or a dip. Ordered islands of VOPc, with (1x1) epitaxy, grow on the FePc layer at submonolayer coverages. The individual VOPc molecules are imaged in STM with a central depression that would, according to conventional wisdom, imply that V=O points down into the surface. More significantly, however, the STM images show that the VOPc molecules occupy sites directly atop the underlying FePc molecules, and not offset as is the case in the bulk structure of (single) phthalocyanines (including VOPc that forms offset head-to-head double layers in the bulk). The VOPc-atop-FePc geometry strongly implies significant intermolecular bonding, only possible if the V=O points down into the surface, allowing a Fe-O bond to form.



Surface structure and morphology of bimetallic alloys and nanoalloys: insights from numerical simulations

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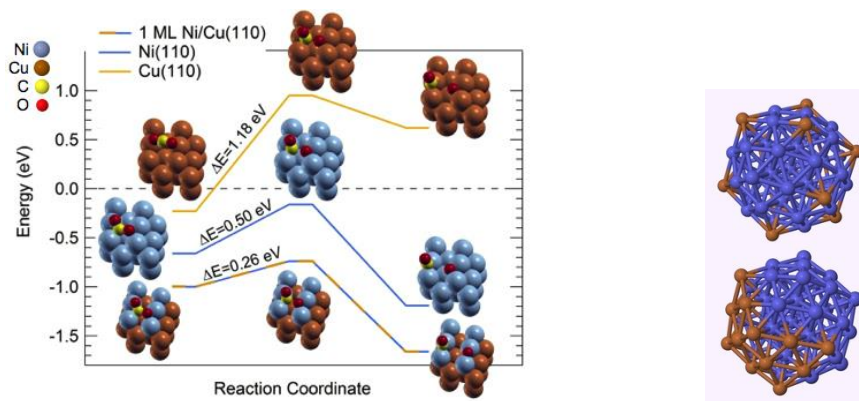
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The nanoscale structure of binary alloys is a key parameter that can be used to tune their properties for applicative purposes, such as for instance in catalysis, to improve reaction rates and selectivity. A representative case is the Ni-Cu system: its surface, whose local composition is crucially determined by segregation thermodynamics and kinetics, exhibits properties that are different from those of the constituent metals and from a simple linear interpolation (Figure) [1].

Nanoparticles, with low-coordination sites and finite-size effects, show different and often more convenient properties than single-crystal surfaces [2]. A further degree of freedom is offered alloying at the nanoscale. Alloy-based nanoparticles, or nanoalloys, show a fascinating variety of composition- and size-dependent structures and morphologies [3].

Numerical simulations based on complementary and different approaches, from quantum-mechanical to semiempirical potentials, combined with surface science experiments, allow to enter into the richness of structures and properties at the atomic-scale.



Left: Calculated energy diagram of CO₂ dissociation on the (110) surface of a bimetallic NiCu alloy and of the corresponding pure metals [2]. Right: Two different homotopes of a Cu₁₂Ni₄₃ icosahedral nanoparticle.

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Structure and phase separation in ultrathin bimetallic alloys

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Intermetallic alloys are of interest for their structural, chemical and magnetic properties. Among them, Fe-Ni alloys have a special place. The rich Fe_{1-x}Ni_x phase diagram as a function of stoichiometry and temperature features a region of immiscibility at around the invar composition $x_{\text{Ni}} = 0.30$. However, due to the suppressed mobility, the phase separation is hindered in bulk samples [1]. Here, we show that Fe-Ni thin films grown on W(110) display a pronounced structural separation at moderate temperatures (at around 300 °C) near the micron scale (figure – left). Interestingly, the fcc-bcc coexistence can be observed down to the monolayer limit [2]. The Ni-enrichment on the surface and the high surface diffusion are found to be responsible for the observed microstructure. Furthermore, time-resolved measurements as a function of temperature indicate that the rate-limiting energy barrier is about 1.6 eV (figure – right). We identify this barrier with the vacancy-formation energy in the bcc phase. I will conclude the presentation with a discussion of the magnetic state of the hetero-structured film.

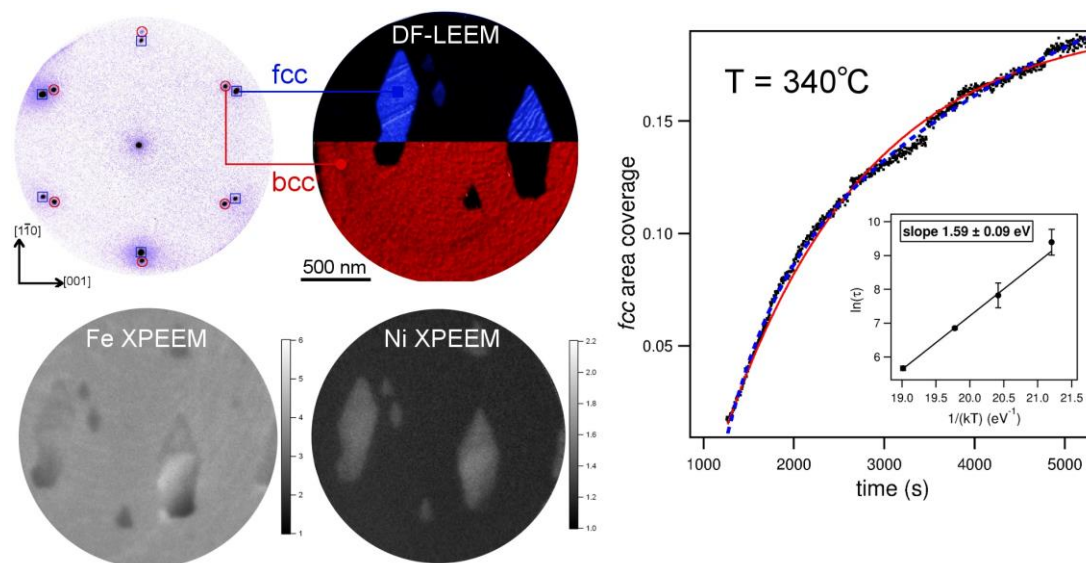


Figure: (Left) LEED, dark-field LEEM and XPEEM data of the fcc-bcc phase-separated Fe-Ni film on W(110). (Right) The temperature-dependent dynamics of the phase-separation indicates an energy barrier of about 1.6 eV.

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Modelling of STM-induced diffusion of hydrogen interstitials in the Pd(111) near-surface region

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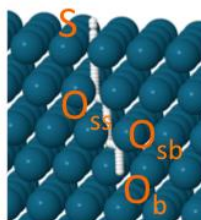
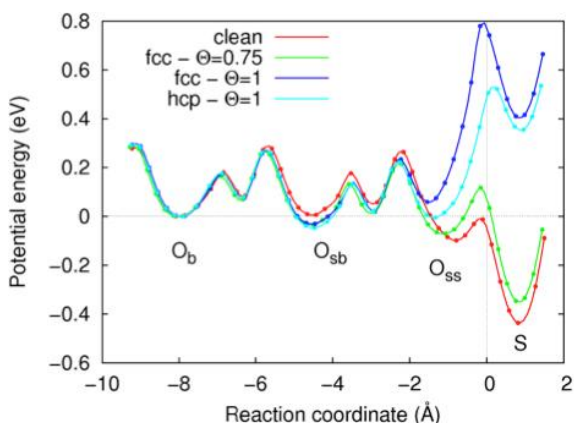
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There's STM experiments have shown that it is possible to manipulate buried [1] and adsorbed [2] H on Pd(111) to produce nanopatterned surface structures of PdH_x composition. Although the experimental observations point to occupation of the subsurface sites (O_{ss}), the actual distribution of H in the manipulated regions is unknown. The factors determining the diffusion of H are: inelastic collisions with STM electrons, H-H interactions, and tip effects in the form of electrostatic fields. We have studied these three factors first at a static level, by DFT evaluations of the potential energy surface (PES) of a H interstitial at the surface region [3], and then at a dynamical level. In the latter, we use a new quantum-mechanical model of the non-adiabatic coupling (NAC) between the H vibrational states with their metallic embedding electron density, which accounts for the electronic structure details of the Pd Fermi surface [4]. The static study rules out significant electrostatic effects for typical STM bias voltages, $V < 2$ V, but shows that H precoverage strongly modifies the PES around the O_{ss} site (see Figure). Surface, S, sites are energetically favoured by 280-340 meV and resurfacing is likely whenever empty S sites are available, with barriers < 200 meV. The NAC model



for H transfer rates evidences this strong preference for resurfacing of buried interstitials for voltages and tunnelling intensities up to $V = 1$ V and $I = 1$ nA, respectively. It also shows that at saturation O_{ss} sites are also depopulated towards deeper sites. Most importantly, at long times (~ 100 ns) the system behaves *quasi-thermally*, and the site population dynamics can be

described in terms of effective equilibrium constants.

Figure: One-dimensional PES for H in the near-surface region of Pd(111) for surface site coverages $\Theta=0-1$.

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Structure and dynamics of two-dimensional layers with low energy electron microscopy and nano-diffraction

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Low energy electron microscopy and nano-low energy electron diffraction offer unique and complementary capabilities for studying the structure and dynamics of inhomogeneous surfaces, thin films and two-dimensional layers with high spatial/temporal resolution. These diverse capabilities will be demonstrated by studies of the defect structure of graphene(g)/metals and anomalous diffusive dynamics of the Pb wetting layer on the Si(111) surface. The prevalence of defects in large-area graphene fabricated on metal substrates is of interest because it may undermine the unique physical and electronic properties that are vital to its use in technological applications. Our investigations reveal the proliferation of lattice orientational disorder and small angle grain boundaries in g/Ru(0001) [1]. On the contrary, incommensurability and polymorphism are observed in graphene that exhibits greater orientational uniformity (Fig. 1). Two-dimensional strain mapping in g/Ir(111) reveals inhomogeneous strain relaxation by wrinkles that form due to lattice mismatch with the substrate (Fig. 1). This suggests that it may be possible to strain engineer the properties of graphene if wrinkling can be controlled to form desirable wrinkle networks. Diffusion dynamics in Pb/Si(111) was investigated by monitoring the relaxation of non-uniform coverage profiles prepared by laser induced thermal desorption [2,3]. The sensitivity of diffraction satellite peaks produced by the wetting layer to its density is exploited to determine local Pb coverage with 0.001 monolayer precision using nano-LEED. Profile evolution observed in real-space and detailed coverage profiles extracted from reciprocal-space features contradict expectations of classical gradient-driven mass flow. Instead, they suggest an exceptional collective super-diffusive mechanism, whereby the Pb layer slides cohesively over the substrate surface.

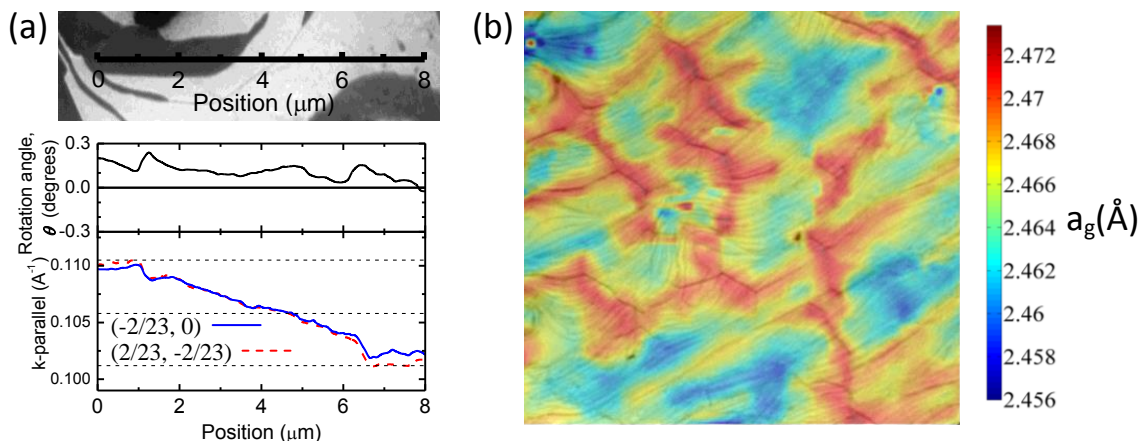


Figure: (a) Lattice rotations, incommensurability and polymorphism in g/Ru(0001) and (b) localized strain relaxation near wrinkles in g/Ir(111) are obtained from moiré diffraction peak positions using nano-LEED.

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Comparing graphene growth on Cu(111) vs. oxidized Cu(111)

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The epitaxial growth of graphene on catalytically active metallic surfaces via chemical vapor deposition (CVD) is known to be one of the most reliable routes towards high quality large-area graphene. This CVD-grown graphene is generally coupled to its metallic support resulting in a modification of its intrinsic properties. Growth on oxides is a promising alternative that might lead to a decoupled graphene layer. Here, we compare graphene on a pure metallic to graphene on an oxidized copper surface, in both cases grown by a single step CVD process under similar conditions. Remarkably, the growth on copper oxide – a high- k dielectric material – preserves the intrinsic properties of graphene; it is not doped and a linear dispersion is observed close to the Fermi energy. Density functional theory calculations give additional insight into the reaction processes and help explaining the catalytic activity of the copper oxide surface [1]

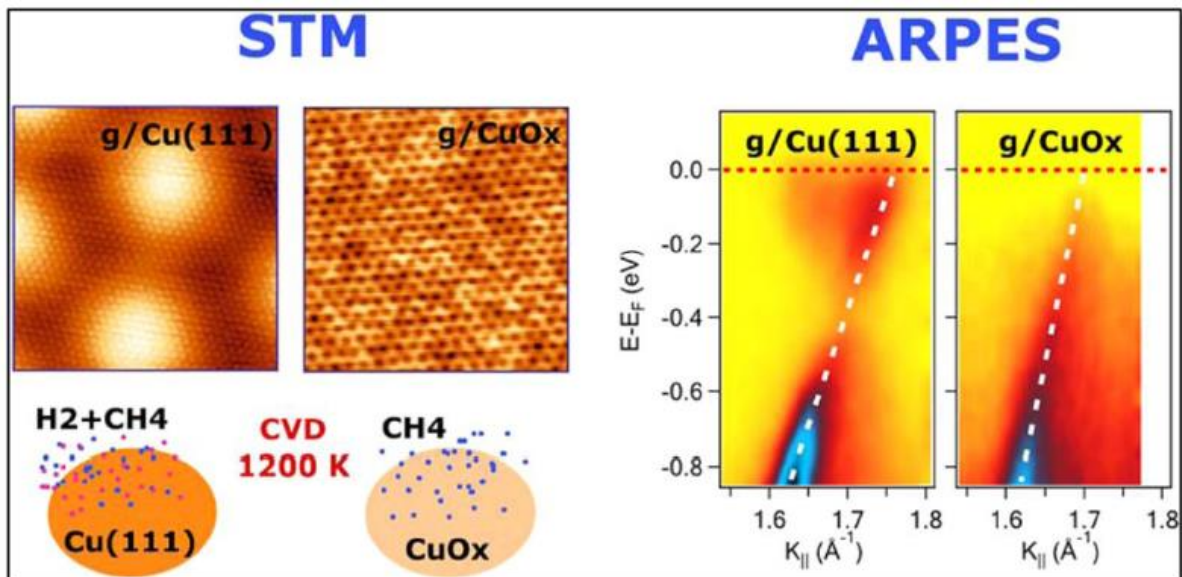


Figure: STM and ARPES measurements comparing graphene grown on Cu(111) and oxidized Cu(111), respectively. In both cases, graphene was grown in a single step CVD process.

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Fast STM observations of catalytic surface reactions: CVD graphene growth on Ni

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Chemical Vapour Deposition (CVD) is a well-established method to produce high quality 2D materials, such as graphene, hexagonal boron nitride and metal dichalcogenides. An effective large-scale application of these materials calls for a deep understanding of their growth processes in order to improve their quality and tailor new functionalities. In the case of graphene, while the growth mechanisms at the micro-scale were clarified by a number of experimental investigations [1,2], little is known on their details at the atomic level, due to technical limitations in observing the growing islands with sufficient spatial and temporal resolutions.

We investigated the graphene growth on a Ni(111) surface by means of a Variable Temperature Scanning Tunnelling Microscope (VT-STM) coupled to a Fast STM module that provides video-rate acquisition capability [3].

As a first step, we characterized the edge structures [4], which play an important role in the growth processes, supplying the active sites for the attachment of new atoms. Combining the experimental results with density functional theory (DFT) calculations, we reveal the importance of the metal substrate in breaking the symmetry of adjacent edges and evidence the formation of covalent bonds between the terminal C atoms and the underlying Ni atoms during the growth process. Upon cooling to room temperature, however, background H₂ molecules dissociate on the Ni surface and H atoms bind to the terminal C atoms, detaching the edge from the substrate.

In a second step, for the first time we investigated by *in-situ* video-rate STM the growth mechanism of epitaxial graphene islands on Ni. Real-space, atomically resolved measurements allow us to identify the active sites for C attachment on different edge structures and to unravel the catalytic role of metal adatoms [5].

These findings reveal the capability of our approach to unveil essential details of atomic scale dynamical processes occurring at surfaces.

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Atomic structure of one-dimensional metal-oxide hybrid chains formed on the Ir(100) surface

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Oxide structures with reduced dimensionality show significantly different properties compared to their bulk counterparts which lead to a special interest in this kind of systems in the field of nanotechnology. Prerequisite for any application is the controlled growth and the knowledge of the exact structure of such low dimensional systems. Here, we present the self-organized growth of one-dimensional cobalt oxide nanowires on the Ir(100) surface, which form after the deposition of 1/3 ML cobalt under oxygen rich conditions and elevated temperatures. Depending on the oxidizing agent (O_2 or NO_2) nanowires of either CoO_2 or CoO_3 stoichiometry can be formed. Even more, both oxidic wires can be completely reduced by hydrogen to give a ordered, purely metallic Ir_2Co surface alloy. All of these metal and metal-oxide hybrid structures grow as homogeneous 3×1 -periodic domains on the plain Ir(100) terraces. The high degree of lateral order of these one-dimensional structures allows their quantitative characterization by means of full-dynamical LEED analyses.

For each structural phase a huge intensity data basis (between 10,000 eV and 20,000 eV) was collected for normal incidence of the primary electron beam and energies ranging up to 800 eV. The final best-fit structures yield an excellent agreement between experimental and calculated spectra expressed by Pendry R-factors in the range 0.090 - 0.116. Furthermore, all the structural findings are independently confirmed by DFT calculations where the geometric parameters of the respective model coincide with those derived from LEED within the picometer range.

The common structural features of all found phases, namely the CoO_2 -, CoO_3 -stripes and the Ir_2Co alloy, are monoatomic Co wires with a lateral distance of three substrate lattice vectors. In case of the ordered surface alloy these Co wires are embedded in the outermost iridium layer in registry with the adjacent iridium rows. In the oxidized state the situation is very different: The cobalt chains are completely decoupled from the substrate (pulled out by 0.9 Å), shifted by half the substrate's lattice vector and linked only via the oxygen atoms at both sides (as shown in Fig 1). In the case of the fully oxidized CoO_3 phase one additional oxygen atom is located under every Co atom of the wires.

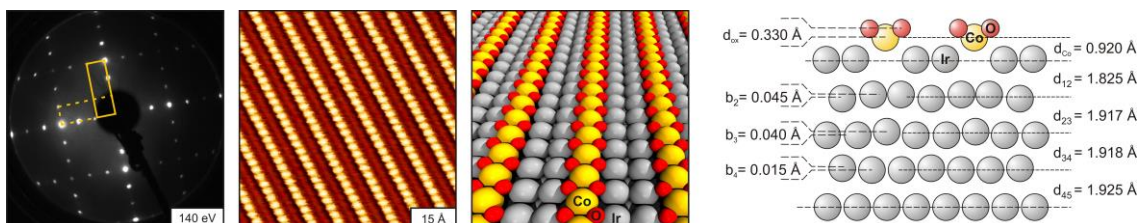


Figure 1: LEED pattern, STM image, ball model and best-fit structure of the Ir(100)- 3×1 - CoO_2 phase

Structure of Epitaxial graphene Moiré coincidence network; lattice mismatch versus surface strain

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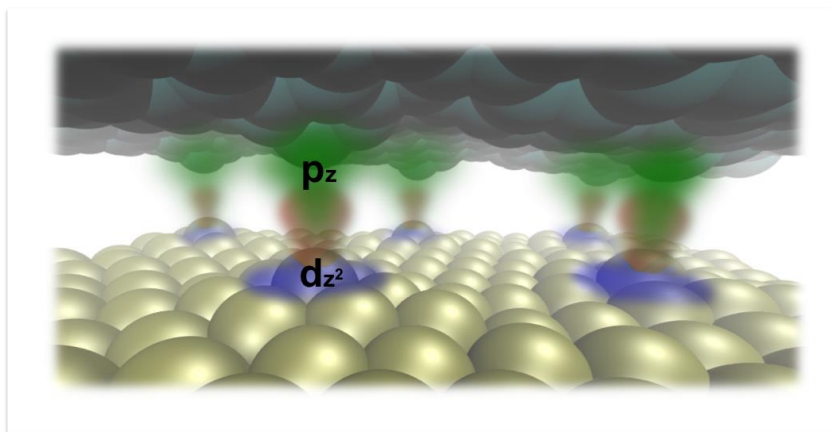
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Epitaxial graphene can be efficiently grown on transition metal surfaces leading to the formation of coincidence superstructures (Moirés) exhibiting different sizes and orientations with respect to the substrate. In this work we aim to understand the modification of the graphene atomic and electronic properties induced by the interaction with the underlying surface. Firstly, we will address the problem of how many Moirés superstructures can be accommodated on a particular metal surface. To this goal, we have grown submonolayer coverage of multi-domain epitaxial graphene islands on Pt(111) by low-temperature decomposition of large organic precursors [1] and observed them by STM. We present a purely simple geometric model that predicts that graphene can only grow at those angles at which the mismatch between the graphene and the metal networks is minimized [2]. This model was developed for the case of Pt(111), and successfully applied to other metals and found to work with most substrates [3]. However, there are several aspects that remain unclear, as why the mismatch, and not the strain, is ruling the stability of these structures. We have performed full DFT calculations that lead us to the conclusion that for all reported Moirés the system relaxes inducing a non-negligible atomic corrugation both, at the graphene and at the outermost platinum layer [4].



Formation of an anti-Moiré network of pinning points.

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Moiré patterns formed by hexagonal coincidence lattices: applications for metal supported graphene and related materials

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The current interest in graphene (g) and similar 2-dim materials supported on transition metal (TM) surfaces has raised again an old question: "Which moiré phases are observed when placing hexagonally arranged overlayers on hexagonally packed surfaces?" Especially the question occurs, whether or not moiré phases are commensurate and if so, what is the size and the correct indexing of their unit cell. Usually, trial and error methods are used to solve these questions. While for supported g an analytical description could be applied for a special case,[1-2] we derived a geometric construction in a more general way identifying spatial beating frequencies generated by two coinciding and arbitrarily oriented hexagonal lattices.[3] Our analysis delivers solvable analytic equations that predict whether or not first or higher order commensurability may occur which can be visualized as shown in Fig. 1. The displayed graphs indicate where commensurability of 1st and 2nd order spatial beating frequencies may occur within the parameter space of moirés that apply to g/Pt(111). The left axis represents the lattice constant ratio x and the horizontal axis the rotational angle φ of the two coinciding lattices. Yellow patches indicate, where true commensurability is reached. The unit cell can be indexed by a vector $(m,n)_{TM}$ relating to the TM- support lattice (TM=Pt(111)) and at the same time by a vector $(r,s)_g$ relating to the graphene lattice. The colored curves sketched in red/dark-blue $((m,n)_{TM})$ and green/light-blue $((r,s)_g)$ represent the solutions of an analytical expression that leads to the correct indexing. Where such lines cross each other, commensurate cells can be observed as shown for the reported R19.2° and the R23.4° moirés of g/Pt(111). Our approach is universal and may be used for the description of moiré patterns formed on other hexagonally arranged thin layers on any hexagonally packed support surface.

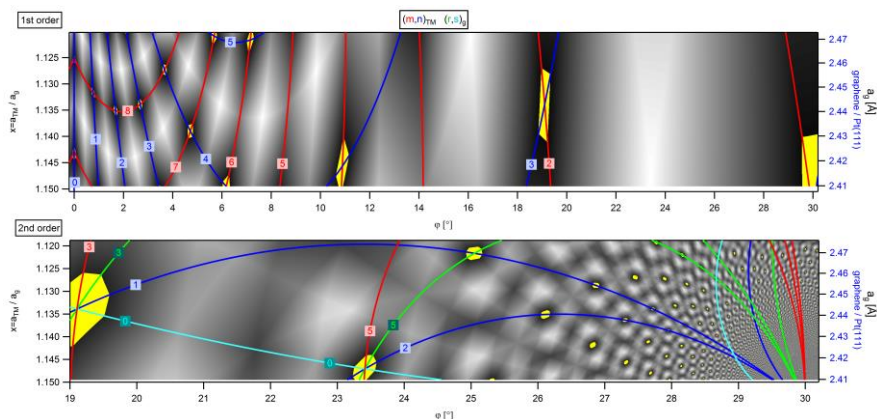


Figure: First and second order commensurability plots indicate possible unit cells for g-Pt(111). In particular, the indexing of the reported R19.2° and the R23.4° moiré pattern as a result of our analytical treatment is shown.

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Theory of Moiré Patterns Found for Graphene and Other Overlayers at Metal Surfaces

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Complex overlayer structures at single crystal surfaces have been observed where long-range order, expressed by additional approximate surface periodicity with very large unit cells, was found. Examples are Pb(111)+C₆₀ near (√(403/7)×√(403/7))R22.8° [1], Ag(111)+3S near (√7×√7)R19.1° [2], or graphene at different hexagonal metal surfaces, such as Ir(111) [3]. This phenomenon can be characterized by spatial interference resulting in 2-dimensionally periodic moiré patterns which consist of similar local surface regions (moirons). We have generalized a previously proposed formalism [4] of determining such moiré patterns based on concepts of higher-order coincidence (HOC) lattices together with 2-dimensional Fourier theory. The extended formalism provides simple mathematical relations allowing to compute 2-dimensional moiré lattices of any order in their dependence on layer rotation and scaling with respect to a given HOC lattice structure. The theoretical findings will be illustrated by animated graphics by as well as by results from experimental studies. For isotropically scaled (p × p) overlayers the general formalism confirms a singularity near p = 1 resulting in very large moiré lattices observed for graphene on hexagonal metal substrate where the measured moiré lattice constants [3] agree quantitatively with theory. For rotated (1 × 1) Rα overlayers the formalism yields a singularity for α = 0° which confirms the large moiré lattices found for superimposed graphene layers with the measured moiré lattice constants being reproduced by the present theory. Moirion lattices resulting from combined isotropical scaling and rotation, observed for C₆₀ at Pb(111) [1], can also be quantitatively accounted for by the present formalism. Further, the formalism can explain giant moiré lattice shifts due to overlayer shifting which occurs for graphene at stepped metal surfaces [3].

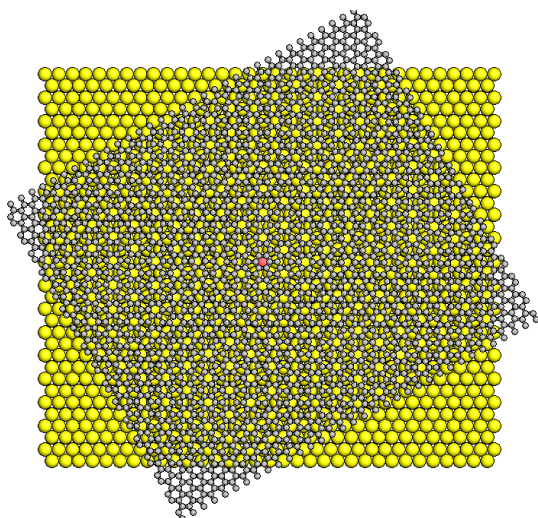


Figure: Second order moiré pattern of adsorbed graphene at Ir(111) described as Ir(111)+(0.906 × 0.906)R29.5°-Graphene. Yellow balls refer to Iridium, gray balls to carbon.

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Ultrafast charge transfer at boron nitride monolayers on variably coupled substrates.

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The dynamics of charge transfer at surfaces is very important for many processes occurring in photochemistry and electrochemistry. As it is likely to contain tunneling steps, it is expected to be connected with the overlap of states at the surface, as well with the connectivity to the substrate. In the case of well-defined monolayers both are expected to contribute. Previously, we have reported detailed results for ultrafast charge transfer at graphene (Gr) monolayers on substrates with strongly varying coupling [1]. The very fast timescales can be nicely measured by the core hole clock method [2] with adsorbed argon, which effectively tests the lifetime of an excited electron on a resonantly core-excited Ar adsorbate (a transient quasi-potassium atom in front of the surface). Using this technique, we have shown previously that the charge transfer (CT) times at Gr surfaces lie in the low femtosecond range and vary by more than a factor of 6 between the strongly coupled valleys for Gr/Ru(0001) and various types of quasi-freestanding Gr; other cases are in between. For the corrugated Gr layers on Ru and Ir, we were able to separately measure the CT on the valleys and the hills; they clearly differed.

We have now done the same measurements on variably coupled BN layers. This appeared of interest since Gr and BN monolayers are isoelectronic and have the same geometry, but have very different electronic structures, Gr being a zero-band gap semiconductor with Dirac electrons, and BN an insulator with wide band gap (5.8 eV) and normal electrons [3]. The experiments were carried out at the SuperESCA beamline of the Elettra lightsource in Trieste. BN on Ru(0001), Ir(111), Ni(111), and Cu(111) were investigated; for Ru and Ir, hills and valleys have been separated. Somewhat surprisingly we find that in many cases the data are quite similar to those on Gr [1]. This suggests that the predominant effect for the CT is the penetration of the substrate orbitals through the Gr or BN monolayers. We also see strong effects of the band structure. The results will be discussed.

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Monday, October 19, 18:00.

ECSCD-12: Poster Session

Exploring novel nanoporous anodic alumina layers obtained from ionic liquid analogues electrolytes

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Nanoporous anodic alumina layers have been widely investigated and used in various applications including optical sensor and biosensors development, as templates, filters, corrosion protection coatings or for decorative purposes by colouring.

Usually they can be obtained through aluminium anodization involving aqueous acidic or alkaline electrolytes and the nanostructural features are mainly determined by the selected electrolyte and the applied anodization potential. Therefore, the development of novel electrolytes would expand the applicability of anodic alumina.

In the last years, a green chemistry based on ionic liquids (ILs) gained a wide recognition as potentially benign solvents and widespread application. In addition the use of a novel class of ionic liquids based on eutectic mixtures of quaternary ammonium salts with hydrogen bond donor species attracted recently an increased interest. These media, also known as “deep eutectic solvents (DES)” or “ionic liquid analogues (ILAs)” exhibit good air and water stability, may be easily synthesized at a lower cost. They are potentially recyclable, biodegradable and with no harm on human health.

Thus, the paper presents for the first time several preliminary experimental results regarding the growth of novel self-ordered nanoporous anodic alumina using ILAs based on eutectic mixtures of choline citrate, able to produce quite compact, uniform, aluminium anodic oxide layers. Distances between pores of 130-200 nm have been determined depending on the electrolyte type and anodization conditions.

Based on AFM, SEM, XRD and micro-Raman spectroscopy investigations, the influence of anodization parameters (e.g., electrolyte composition, applied anodization potential and current density, anodization duration, applied thermal treatment) on the final structural characteristics of the anodic layers are discussed.

Acknowledgment: We acknowledge funding from NANOCOATIL project, Contr.No.7-082/2013 under M ERA Net Program.

High-pressure-high-temperature synthesis of new metastable phases Bi_2Te_3 , Sb_2Te_3 and Bi_2Se_3 topological insulators with surface superconductivity

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We synthesized for the first time bulk polycrystalline samples of new metastable phases of Sb_2Te_3 , Bi_2Te_3 and Bi_2Se_3 topological insulators by a rapid quenching after a high-pressure-high-temperature treatment at pressures of 4 GPa and 7.7 GPa in the temperature range of 873 - 1573 K and investigated their structure, electrical and magnetic properties in the temperature range 0.5-300 K. The crystal structure of metastable phases was investigated by X-ray powder diffraction and electron microscopy diffraction analysis. X-ray diffraction patterns were fitted by Rietveld profile matching using the FULLPROF-program. At each refinement cycle, the fractional coordinates, scale factor, isotropic thermal parameters, profile function and cell parameters were optimized. Atomic coordinates were calculated using full profile X-ray diffraction pattern analysis and *ab initio* calculations. Two metastable phases of *m*- Sb_2Te_3 and *m*- Bi_2Te_3 quenched after HPHT treatment at $P = 4 \text{ GPa}$; $T = 873 \text{ K}$ and $P = 7.7 \text{ GPa}$; $T = 973 \text{ K}$ have been found. The first of them, *m*- Sb_2Te_3 is quite stable at ambient conditions. Its crystal structure is monoclinic ($C2/m$) with the cell dimensions: $a=15.644(80) \text{ \AA}$, $b=4.282(8) \text{ \AA}$, $c=9.382(20) \text{ \AA}$, $\beta=89.70(5)^\circ$ [1]. The reliability factors are: $R_{\text{Bragg}}=0.12$, $RF=0.13$, $\chi^2=4.35$. There are two different types of Sb atoms: with seven-coordinated by Te atoms for Sb1 and for Sb2 – eight-coordinated by Te atoms forming composite coordination polyhedra. Polyhedra are repeated along *b* axis forming an infinite band. The structure of *m*- Bi_2Te_3 phase quenched after treatment at $P = 7.7 \text{ GPa}$; $T = 973 \text{ K}$ is rhombohedral ($R3m$, sp.g. No 160), the lattice parameters are: $a=4.42 \text{ \AA}$, $b=29.84 \text{ \AA}$ [2]. *m*- Bi_2Se_3 , phase quenched after treatment at 7.7 GPa and 1473 K, has partly amorphized monoclinic primitive structure with 8-coordinated Bi-atoms which may produce infinite chains.

Unlike pristine material, the quenched metastable phases of Sb_2Te_3 and Bi_2Se_3 possess superconductivity transition with $T_C^{\text{onset}} = 2.5 \text{ K}$ at normal pressure and $T_C^{\text{onset}} = 7 \text{ K}$ in Bi_2Te_3 . The low critical current value of about 2 mA in the metastable Sb_2Te_3 phase and an absence of the detectable heat capacity effect at the superconducting transition indicate a low-dimensional character of the superconductivity which may refer to the surface of the crystal grains. The zero-field magnetic susceptibility cusp and linear positive magnetoresistance indicate the topological insulator state. Thus metastable phase of Sb_2Te_3 topological insulator obtained by high-pressure-high-temperature treatment possesses surface superconductivity at normal pressure and may be interesting for Majorana fermions search. Models of the surface structures are suggested and the DOS, band structures are calculated.

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**The FAST module: an add-on unit for driving commercial scanning probe
microscopes to video rate and beyond**

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We present the design and the performance of the FAST (Fast Acquisition of SPM Timeseries) module, an add-on instrument that can drive commercial scanning probe microscopes (SPM) at and beyond video rate image frequencies. In the design of this module, we adopted and integrated several technical solutions previously proposed by different groups in order to overcome the problems encountered when driving SPMs at high scanning frequencies. The fast probe motion control and signal acquisition are implemented in a way that is totally transparent to the existing control electronics, allowing the user to switch immediately and seamlessly to the fast scanning mode when imaging in the conventional slow mode. The unit provides a completely non-invasive, fast scanning upgrade to common SPM instruments that are not specifically designed for high speed scanning. To test its performance, we used this module to drive a commercial scanning tunneling microscope (STM) system in a quasi-constant height mode to frame rates of 100 Hz and above, demonstrating extremely stable and high resolution imaging capabilities. The module is extremely versatile and its application is not limited to STM setups but can, in principle, be generalized to any scanning probe instrument.

Studying strained 2D materials by two-probe STM-AFM.

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The 2D materials have large Young's modulus, low residual stress and spectacularly large breaking strength as well as their interesting and unique electrical properties as compared with 3D materials [1]. Strain applied on 2D layers can be used to tune electronic band structure of the 2D materials [2]. The deformation of layered structures has already been studied, but the samples used in experiments were either not free-standing, or the same probe that is used for generating strain is simultaneously used for spectroscopy [3]. On the other hand, although there are many studies on band structure of graphene, there is not much experimental work on the effect of strain influencing electronic band structure of few layer graphene [4]. In the presence of strain in 2D materials (MoS₂ and graphene), while band structure of MoS₂ is changed, the spin orbit induced band gap is observed in graphene [5].

In this study, the effect of deformation on 2D materials has been investigated by a Double-tip Scanning Probe Microscope (DXSPM). The effect of out of plane deformation induced by STM tip on free standing graphene has been reported previously and it has been shown that graphene membrane follows the STM tip during deformation instead of vice versa [6]. A new and unique setup comprising AFM and STM scanners enables to deform 2D materials using one of the tips and the other tip is used to measure of electrical and structural properties of 2D materials. Furthermore, we have investigated local electronic and mechanical properties of the strained 2D materials by a hybrid AFM/Raman spectroscopy system. The local forces applied by AFM tip on a MoS₂ layer have led to large Raman shift in A_{1g} (out-of-plane) mode when E_{2g}¹ (in-plane) mode indicates very small shift across applied force in our experiments.

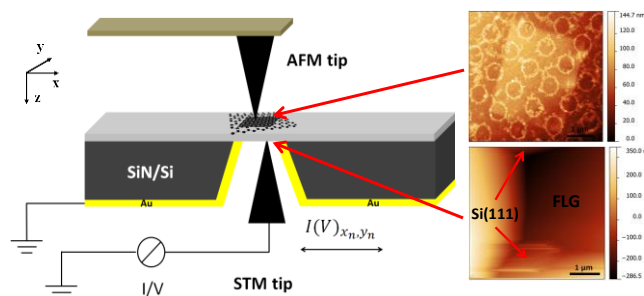


Figure: Imaging FLG (few layer graphene) membrane from both sides simultaneously via AFM and STM.

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On the Cobalt intercalation between graphene and Ir(111)

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Magnetic hybrid systems are currently studied because of their possible use as magnetic memories. In this context, Cobalt (Co) films, with a thickness smaller than 10nm, deposited on Iridium (Ir) substrates show perpendicular magnetic anisotropy (PMA), crucial for the development of new ultra-high density memory devices [1]. When dealing with such thin films, the oxidation of the magnetic layer can compromise the magnetic behavior of the whole system. A graphene (Gr) capping layer can be used to lower the Co chemical reactivity and prevent its oxidation.

Gr/Co/Ir(111) systems can be obtained by deposition of Cobalt onto Graphene covered Iridium (Gr/Ir) followed by an annealing promoted Co intercalation through the Gr layer. This procedure results also into hybrid systems with an enhanced PMA [2]. The intercalation process is relatively straightforward but the high temperatures (500K) required to drive it may affect the Co/substrate interface and its magnetic behavior. A detailed characterization of structure and morphology is then mandatory to reliably understand the structural evolution upon the intercalation and its effects on the magnetic response.

Here we report on a deep investigation of Gr/Co/Ir(111) and Co/Ir(111) systems. From the comparison of the two systems one can distinguish the graphene-induced modifications in the magnetic response. Complementary probes were employed in order to investigate the magnetic properties (MOKE) and structural features (Surface x-ray diffraction, LEED, XPS, and STM). Our results prove that the magnetic properties of the thin Co films depend on atomic scale modifications which can be induced by thermal treatments: even subtle changes to the preparation conditions of Gr/Co/Ir can cause severe modifications to the structure of the Co-Ir(111) interface and then to the magnetic response of the final device [3].

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Trapping of charged gold adatoms by dimethyl sulfoxide on a gold surface

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We report the formation of Dimethyl Sulfoxide (DMSO) molecular complexes on Au(111) enabled by native gold adatoms unusually linking the molecules via a bonding of ionic nature, and, at the same time, anchoring the cluster to the substrate. DMSO is a widely used polar, aprotic solvent whose interaction with metal surface is not fully understood. By combining X-ray photoelectron spectroscopy, low temperature scanning tunnelling microscopy, and density functional theory (DFT) calculations, we show that DMSO molecules form complexes made by up to four molecules arranged with adjacent oxygen terminations. DFT calculations reveal that most of the observed structures are accurately reproduced if, and only if, the negatively charged oxygen terminations are linked by one or two positively charged Au adatoms. A similar behavior was previously observed only in non-stoichiometric organic salt layers, fabricated using linkage alkali atoms and strongly electronegative molecules. These findings suggest a novel motif for anchoring organic adlayers of polar molecules on metal substrates and also provide new insight into the interaction of DMSO with gold.

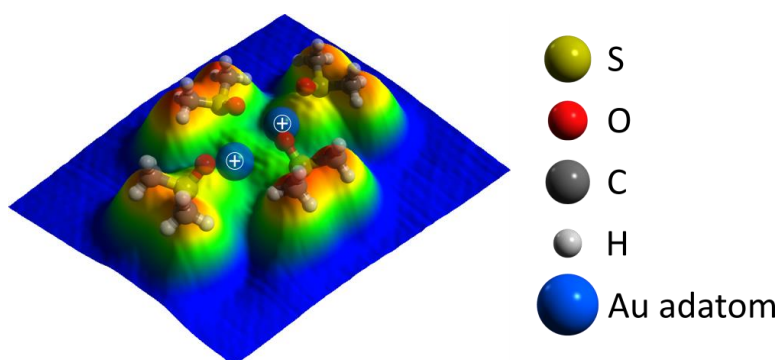


Figure: a scanning tunneling microscopy image of a DMSO complex made of four DMSO molecules entrapping two charged gold adatoms.

Hydrogen capture by porphyrin macrocycles at the TiO₂(110) surface

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The reactivity of porphyrin and phthalocyanine macrocycles is affected both by the composition and by the structure of the supporting surface, and can be either enhanced^[1] or attenuated^[2] by a suitable choice of the substrate. Most of studies at the atomic scale focused on metallic substrates, but model catalysts such as titania surfaces offer a much larger number of degrees of freedom for chemical reactions to take place. In fact, a few seminal studies of the contact layer of phthalocyanines and porphyrins on the rutile TiO₂(110) surface have been reported in the literature, where x-ray photoemission measurements have shown a large and unexpected core level shift of the nitrogen peaks, which interpretation is controversial. In our investigation (XPS, NEXAFS, STM, DFT), we demonstrate the chemical origin of the nitrogen core level shift, as due to the bonding of hydrogen to the iminic nitrogen of metal-free porphyrins, which takes place at room temperature. We additionally show that this enhanced reactivity towards hydrogen capture is due to the interaction of the tetra-pyrrolic macrocycle with the TiO₂(110), independently of the different functional terminations of the porphyrin molecules. Our findings can be extrapolated to the case of phthalocyanines, including their metalated homologues, thus concerning a wide family of systems for perspective applications (catalysis, energy conversion, etc).



Figure: Porphyrins adsorb with the macrocycle parallel to the TiO₂(110) surface atop the protruding oxygen-bridge rows, where hydrogen uptake from the substrate fully hydrogenates the tetra-pyrrolic macrocycle.

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Recovery of surface morphology during growth from diffraction intensities

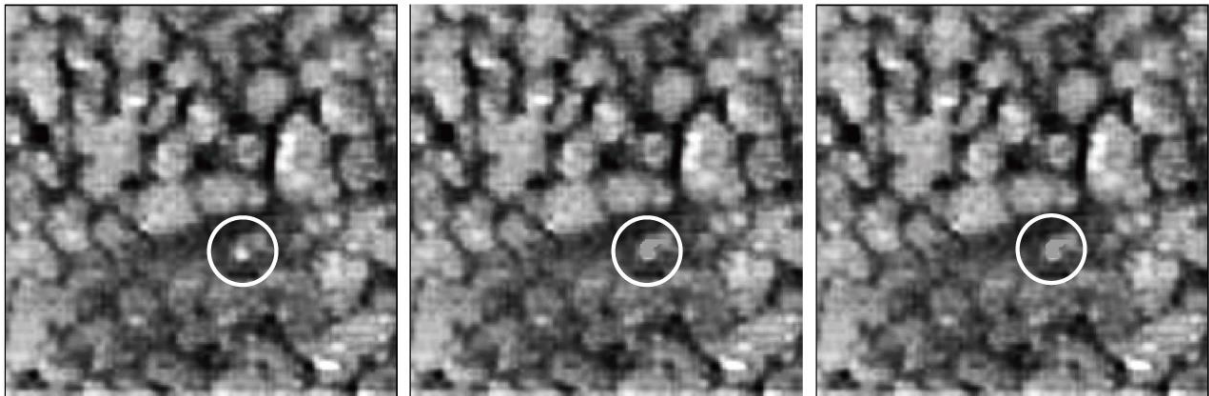
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The specular beam intensity of RHEED (Reflection High Energy Electron Diffraction) has been widely used for monitoring growth in a layer-by-layer fashion. In order to directly observe surface morphology, we need special equipment such as REM (Reflection Electron Microscopy) and LEEM (Low Energy Electron Microscopy). It should be quite useful to develop a method for recovering surface morphology in real time from measured diffraction intensities.

We have studied such a method suited for recovering surface morphology especially during growth from diffraction intensities by extending the phase retrieval algorithm [1,2]. Diffraction intensities used in this study are not the Bragg intensities but scattered electron intensities within a whole Brillouin zone. It is assumed that the size of the surface is finite and the change in the surface morphology from one time to the next is small. Then a kind of perturbation approach can be applied to recovering the surface morphology at the next moment very quickly and precisely. It is an advantage for recovering surface morphology during growth or during any dynamic variations that we have a known morphology at one time as a reference. One test example is shown in the figure below. The change in the morphology occurs around a small (bright) island within the circle. The left figure shows the reference morphology. The middle and right figures show the modified morphology and the recovered morphology by using the present approach, respectively. The agreement between the middle and the right figures is excellent and the phase retrieval is successful. We will discuss how precisely we can recover surface morphology by this approach and necessary condition for the application.



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Oxygen adsorption on Fe(110) revisited

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For years, oxygen adsorption on iron surfaces attracted a lot of interest because of its importance in oxidation, passivation, corrosion and, recently, in metal-oxide tunnel junctions for spintronic applications. For the closest-packed Fe(110) surface, which is well suited for the model studies due to its stability and reproducibility, the oxygen adsorption was investigated from the beginning of the surface science [1]. Surprisingly, despite the numerous previous studies we report on new adsorption structures in this system.

Adsorption of oxygen on the (110) surface of epitaxial Fe films on W(110) was studied using low energy electron diffraction (LEED), low energy electron microscopy (LEEM) and Auger electron spectroscopy (AES), within the exposure range 0 – 300 Langmuir (L). Selected oxygen adsorption structures on Fe(110) reported in the literature were critically compared and revised in reference to the present study. Initial adsorption of $\frac{1}{4}$ oxygen monolayer (ML) resulting in the commonly observed (2x2) structure was followed by a structure that was frequently termed as (3x1). Its complex LEED pattern was interpreted as coming from two structural domains of a large oblique unit cell (eight times larger than the substrate unit cell) and $\frac{3}{8}$ oxygen coverage. A new (3x2) structure was identified at a coverage of $\frac{2}{3}$. The last two structures were verified in LEEM and confirmed by density functional theory calculations.

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Study of Ni-O system with a charge transfer potential implemented in the LAMMPS code

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Nickel-based alloys are known for their good resistance to oxidation and corrosion phenomena, to which they owe their widespread use in many technological fields such as aeronautics and energy production. Several experimental and theoretical studies have been conducted on this type of alloy with the aim to optimize their performance. A fairly recent experimental study [1] performed on a series of oxidized nickel samples showed an accelerated oxidation process, and this speedup has been associated with presence of defects: native and/or generated during the oxidation process. In order to check the hypothesis, one of us has conducted first-principles calculations on the Ni-O system containing small point defects such as monovacancies and divacancies [2-3]. These calculations pointed to a strong interaction of oxygen dissolved in the matrix with the vacancy. A further hypothesis put forth, as a result, that this type of interaction could explain the experimental findings, and this through a novel diffusion mechanism of oxygen by pairs (oxygen-vacancy). Nevertheless, a first-principles quantum approach to calculations requires significant resources and is unable to permit exploration of the scales of space and time to observe and study the phenomena at play in the system. To remedy this “shortcoming”, the method of molecular dynamics is the preferred one. Compared with quantum approaches, the accuracy of the results of this method is closely related to the quality of the interaction potential used for the description of the system. To this end, we propose to present our results of calculations on the system Ni-O and NiO with a new potential (EAM-CTIP) developed by Zhou and Wadley[4] that we have implemented in the computer code LAMMPS and optimized for a satisfactory reproduction of the behavior of oxygen in solution in the nickel in the presence of vacancies. The results we have obtained concerning the stability of Ni, NiO and oxygen-vacancy complexes, are in good agreement with other experimental and theoretical studies found in the literature

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Metal surface adsorbed Retinoic acid as a Kondo switch

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Retinoic acid (ReA) is member of a class of compounds known to undergo reversible photocatalytic switching in biological systems, thus constituting a promising candidate as an engineered surface-adsorbed molecular switch. Scanning Tunneling Microscopy (STM) experiments on an array of regularly adsorbed ReA molecules suggest four distinct and reversibly switchable states on a Au(111) surface upon inelastic electron tunneling. Further evidence from scanning tunneling spectroscopy (STS) experiments revealed not only a geometric but also an electronic component to these switched states through a Kondo-effect. We introduce a first-principles based systematic study of adsorbate conformations and propose probable adsorption geometries through a detailed screening approach based on dispersion-corrected Density-Functional-Tight-Binding (DFTB) and dispersion-corrected Density-Functional-Theory (DFT). Furthermore, ionization and radical forming processes are investigated using a Δ SCF approach. We present simulated Tersoff-Hamann based STM images and propose an explanation of the Kondo-effect based on the formation of a stable organic radical cationic species (ReA^{**}).

Laser nano- and micro-structuring of silicon using a plasma lens

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Nanostructuring of a metal surface by means of laser irradiation is an area of primary interest in nanotechnology. There is a recent trend to use these type of targets for X-ray generation, ion acceleration and the study of intense plasmonics in high intensity laser-matter interaction. Many studies have been carried on the formation of more or less ordered, or periodic, nanostructures when a metal or semiconductor substrate is irradiated with pulsed laser light. Such structures have been obtained with techniques based on laser scanning microscopes with ultra-short laser pulses by a two beam irradiation of a silicon surface achieved using a Lloyd mirror configuration or by the interference between two or more laser beams.

It must be emphasized, however, that the physics behind such laser-induced surface nanostructuring are not fully understood. So far, none of the mechanisms proposed can fully explain these results. Among the various hypotheses for the formation mechanism of laser-induced short periodic nanostructures in semiconductors, the most accepted one involves the excitation of the semiconductor surface plasmon by the incident laser light, which would occur while the silicon surface is melted. In fact, in these conditions, the free electrons can support the propagation of surface plasmons. The molten surface would adopt a grating-like shape depending on the relation between the wave-vector of incident laser light and the surface plasmon. The rapid cooling after the laser pulse would retain the surface morphology induced during the irradiation.

In this work, we propose a simple plasma lens technique for obtaining a multiple nanostructuring effect without the need of femtosecond laser sources nor a controlled environment. A laser-induced plasma was used as a non-linear optical element for a second laser beam which crossed the plasma perpendicularly to its expansion axis, i.e. perpendicular to the first laser beam. By varying the time delay between the two lasers beams and the fluence of the laser generating the plasma plume, various patterns were induced on the surface of the silicon wafers used. We have distinguished two main sets of experimental conditions that allow the generation of different structuring effects. By setting the time delay between the two pulses so that the processing beam crosses the plasma while it is still in the expanding phase ($\leq 0.1 \mu\text{s}$) a soft structuring is achieved with several ribbon-like structures formed in addition to partially ordered nanoprotusive structures. For long delays ($>1\mu\text{s}$) the processing beam crosses the plasma when its expansion phase is expired and the wave shocked air is detached and traveling freely. Under these conditions the protusive ordered structures remain although with reduced size and increased order. A further interesting nanostructuring effect has been obtained by lowering the pulse energy used to generate the plasma, which results in a reduced plasma plume expansion and the presence of hierarchical ribbons-like structures along with the nanoprotusive structures.

GIXRD characterization of porphyrin thin films

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Porphyrin derivative complexes are ubiquitous molecules in nature. This pervasiveness arises from their special planar structure with a metal atom bound with 4 N atoms in the macrocycle and from a stable π conjugated system. Among the plethora of applications, porphyrins are nowadays used as a photosensitized donor material in organic photovoltaic cells (OPV), because of their large absorbance in the visible region. In organic semiconductors the solid aggregation induces unique optical and electronic-magnetic properties, which often differ from those of single molecules [1, 2]. Differences in the optical absorption have been measured when comparing films with different degree of ordering [3]. To fabricate OPV cells with high power conversion efficiency, η_E , it is crucial to control the crystal structure, crystallinity, and molecular orientation of the thin films used, because the diffusion length of excitons and/or charge carriers, electrons and holes in their crystalline films becomes longer than in their amorphous form. Zinc octaethyl porphyrin (ZnOEP) is the best candidate as an electron donor for the OPV cells, because Zn owns higher photoabsorbance in the visible light, and good efficiencies have been achieved with dyes where porphyrin macrocycles act as π -bridges [3].

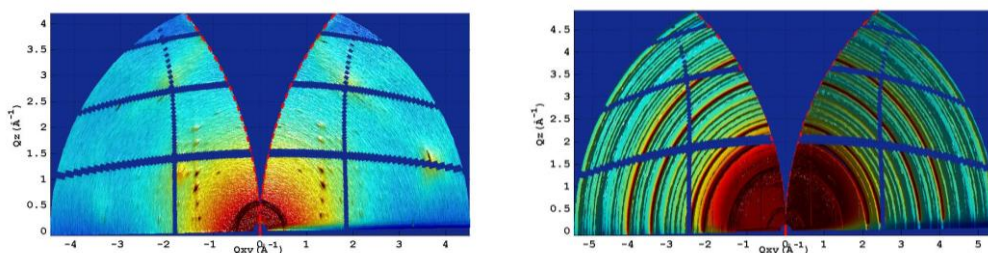


Figure: Bidimensional diffraction patterns on ZnOEP 60 nm films recorded with the 2M Pilatus detector positioned perpendicular to the incident beam. Left: ordered sample on Silicon, right: disordered sample on ITO.

In this work, we present a Grazing Incidence X-ray diffraction (GIXRD) characterization of ZnOEP thin films grown onto Silicon and Indium Tin oxide (ITO) substrates in Ultra High Vacuum and presenting different degrees of ordering. GIXRD ex situ measurements were performed at the X-ray Diffraction beamline 5.2 (XRD1) at the Synchrotron Radiation Facility Elettra in Trieste (Italy). Data show a slight progressive increase in cell volume passing from the less to the more ordered samples, even though hardly exceeding the standard errors. Preliminary peak profile analysis confirms the presence of middle-range order. Simulation of GIXRD patterns is on the way in order to evaluate the prevalent orientation of crystallites even in presence of the additional complexity due to polymorphism.

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A Surface X-ray Diffraction study of the (5x10) NiOEP/Au(111) system

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One of the main challenges of molecular electronics is the controlled growth of the molecular layers on the nanometer scale. In this context the porphyrin self assembled monolayers (SAM) on ordered substrates attract an intense research activity. These systems represent a challenge for surface science, in particular because of the soft nature of the organic material (which can be easily damaged by irradiation), the large number of atoms present in the molecules, and the complex physical chemistry involved in the self-assembly process, though this challenge has been motivated by the appealing technological applications of SAMs that cover many fields of the emerging area of nanotechnology. In this work we present a detailed study of the Nickel Octaethyl Porphyrin (NiOEP) SAMs deposited onto the Au(111) herringbone (HB) surface [1], combining Surface X Ray Diffraction (SXR) and Low Energy Electron Diffraction (LEED). Two different ordered phases of NiOEP on Au(111) have been found: a 5x5 for low coverages with an increased HB periodicity and a 5x10 structure for coverages from 0.7 to 1 ML, with the Au(111) HB recovering its clean value periodicity.

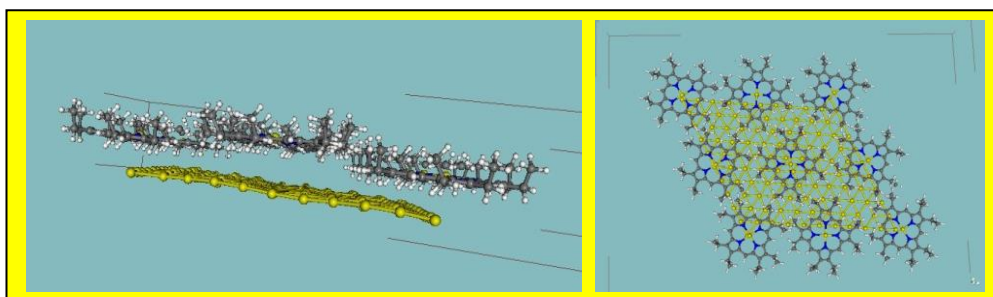


Figure: Side and top views of the (5x10) NiOEP/Au(111) model based on SXR analysis.

The (5x10) phase have been studied in details. The molecular assembly is driven by the molecule-molecule interaction. The unit cell includes two molecules per cell with the ethyl groups oriented upward, in good agreement with STM literature results [2]. Comparison with analogous CoOEP/Au(111) system is discussed [3]. Moreover our analysis enlighten a compression of the intermolecular distances with the intramolecular structure slightly deformed, with the Ni atoms shifted up approximately of 0.15 Å with respect to the N ring plane. The effect of the molecular arrangement in the (5x10) structure is reflected on the orbitals energies [1] and interpreted by means of Density Functional theory.

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Dopant influence on the mechanical stability of telluride amorphous thin films

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Thin films deposition usually possesses a residual stress, which causes limitation in the film thickness, cracking or peeling of the film, or bending of the substrate. The stress is a sum of the thermal stress and the intrinsic stress, appearing in the film during the deposition process. One of the most critical tasks in thin-film technology is to obtain layers free of defects and internal stress. The stress is an important factor, which influences many physical properties as well as the technological performance of the layers. Various methods have been suggested for in situ and ex situ stress measurements. The cantilever technique allows in situ or ex situ determination of the stress by the substrate deflection as the film is deposited onto it. This technique has the advantages of local measurements and high precision due to the small cantilever dimensions.

The glasses in Ge-Te system are attractive materials for infrared optics. They possess wide region of transparency and mechanical stability. By addition of third element in tetrahedral structure of Ge-Te glass one can expect to modify the structure and to optimize materials behaviors.

Thin films from Ge-Te-In(Ga) system deposited by VTE and PLD techniques studied by XRD and SEM techniques revealed homogeneous structure without inclusion of any crystalline phase, composition very close to that of the starting materials, and uniform and smooth surfaces. The intrinsic stress of the thin films with different concentrations of indium or gallium was studied by cantilever bending technique.

All trends observed for the mechanical properties of the chalcogenide materials can be explained with the structural changes occurred after the incorporation of indium or gallium in the glassy matrix.

It was found that all films under investigation were under tensile stress, the appearance of which could be related with the theoretical values of the mean coordination number and some physical and mechanical parameters of the glassy materials, and mainly with the atomic radii of the elements composing the basic structural units. In general, the increase of the density and microhardness of the glassy materials resulted in an increase in the internal stress of the corresponding films.

Structure and behaviours of nickel-cobalt composites

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Mixed transition-metal oxides with a formula $A_xB_{3-x}O_4$ (A, B=Co, Ni, Zn, Mn, Fe, etc.) with stoichiometric or even non-stoichiometric compositions, typically in a spinel structure are members of promising materials family, which attracted increasing research interest worldwide. These oxides due to their remarkable electrochemical properties are expected to play significant roles for low-cost and environmentally friendly energy conversion technologies.

Nickel cobaltite, $NiCo_2O_4$, the spinel mixed-metal oxide shows exceptional ability to serve as an oxygen evolution electrode and has been studied quite extensively by electrochemical methods for the purpose of the Zn-air batteries. However, the oxygen reduction reaction (ORR) on cathode is sluggish which limits the rate performance of the battery. Developing of highly active catalysts for ORR is necessary to improve the performance of zinc-air battery.

The aim of the present work is the study of mixed oxide materials from $Ni_xCo_{3-x}O_4$ system with different additives as bifunctional catalysts for oxygen evolution and reduction electrodes.

The materials are prepared by means of Pechini method and characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), differential thermal analysis (DTA) and scanning electron microscope (SEM). The XRD analysis shows that the oxides crystallize in a cubic spinel phase. The SEM images reveal that the particles are mostly spherical in shape with size between 50-100 nm. The DTA results define the characteristics temperatures of the material.

Primary electrochemical tests characterized the material to be promising for electrochemical application.

Heat-induced formation of molecular coordination networks of porphyrin derivatives on Au(111): Towards dimensionality tuning

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In the fast growing research field of on-surface molecular self-assembly, coordination bonding is currently considered as an important tool for the construction and design of low-dimensional molecular networks on metal surfaces, also in view of their prospective usage in future electronic devices. To date, most of the reported metal-ligand coordination units stabilizing surface-supported metal organic frameworks (MOFs) are based on the combination of organic ligands bearing pyridyl, cyano, hydroxyl or carboxyl endgroups and transition-metal atoms such as Cu, Fe, Co or Ni [1]. However, the construction of such MOFs on Au surfaces with native Au atoms (without adding transition metal atoms) is hardly reported and thus, not well-understood. Here, we show that MOFs comprising porphyrin derivatives can be formed on Au(111) upon annealing. Both a threefold and a fourfold coordination motif stabilizing the MOFs were found. These findings were compared to MOFs made from the same cyano-functionalized porphyrin derivatives and Co atoms. For this, Co atoms and porphyrin derivatives were deposited on Au(111) [2]. In both cases (native Au atoms and additional Co atoms), the same structures were observed what evidences that indeed a coordination bonding is formed between the cyano groups and gold atoms. Moreover, we also investigated the influence of the position of the substituents (cis- vs. trans-isomers) on the MOF formation on Au(111). We could successfully demonstrate that the dimensionality of the MOF can be tuned from 1D to 2D depending on the chosen isomer.

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Dynamical low-energy electron diffraction study of the 5-fold surface of i-Al-Pd-Mn

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A low-energy electron diffraction (LEED) experiment was performed on the 5-fold surface of icosahedral quasicrystalline Al-Pd-Mn at 88 K in order to make a quantitative determination of its surface structure. A large data set with a total energy range of 4500 eV was obtained. A large data set is important for solving complex structures with many parameters. For comparison, data sets for simple surfaces are typically less than 1000 eV, and the largest data set we have ever used, for the Al₁₃Co₄(100) surface, was about 20,000 eV.

The data were analyzed using a "tile-decoration" model based on Henley's canonical cells as the model and using the SATLEED program for the computations. This method has been applied before to other quasicrystalline surfaces [1,2,3]. Earlier LEED experiments on this surface had employed several significant approximations that averaged over the positions of sets of atoms. [4,5]. This is the first LEED analysis for this surface to consider individual atom positions.

The structure is essentially a truncation of the bulk structure, although there are some significant displacements of the surface atom positions from the bulk-like positions. This study represents the most complete study of the surface structure of 5-fold i-Al-Pd-Mn to date, and provides a starting point for more extensive

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High resolution depth profiling of un-doped and Ga-doped ZnO thin films on Si(100) solar cells substrates

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The substitutional doping of ZnO with group III elements, such as Ga, has emerged as a way to obtain high quality transparent conducting oxide (TCO). Its high carrier concentration and wide optical band gap energy of above 3.3 eV has made it to be a suitable material in thin film solar cells. The homogeneity of the depth distribution of the dopant is an important property for applications such as anti-reflective layer of these thin films. Un-doped ZnO and Ga-doped ZnO thin films were deposited by RF magnetron sputtering on wafers of p-type Si (100). Two types of ceramic targets (AJA International, Inc) were employed: un-doped ZnO (99.99%) and ZnO with Ga₂O₃ content of 2 wt% (99.9%). The depth profile analysis of the samples was performed by SNMS (INA-X, SPECS GmbH, Berlín) in high frequency mode (HFM) by using Ar⁺ ions with a fairly low energy for sputtering (E = 200 eV). For the SNMS spectra, analysis the sputtering time was converted to a scale proportional to depth by taking into account sputtering yield changes during profiling and also changes in the layers density. The sputtering rate of each layer was measured separately in preliminary experiments to establish the depth profile calculations. The absolute depth scale was also obtained by measuring the depth of the sputtering crater by profilometric analysis.

The depth profiling of un-doped ZnO presents an intensity of O is observed to be higher at the topmost 3 nm layer of films as a consequence of the contamination of the layer surface due to oxidation in air. Under this thin layer, the oxygen intensity decays slightly during the entire sputtering process. Following the Si signal, a high intensity plate zone is observed from 80 nm in depth indicating the presence of the surface of the substrate. From this same depth a zero intensity of Zn signal is detected, i.e. the ZnO layer thickness is around 80 nm. The depth profile in terms of intensity vs. depth of Ga-doped ZnO thin films was also recorded by SNMS. The intensities related to the main components, i.e. Zn, Si and O, followed the same tendencies than those observed for the un-doped ZnO samples although the O signal decreased slightly more in the un-doped ZnO layer than in the doped one. As a result of this analysis a ZnO layer thickness about 80 nm in-depth was estimated being in accordance with TEM analysis [1]. Besides the mentioned elements, a constant Ga signal was also detected indicating that Ga used as a dopant element was well-distributed throughout the entire ZnO layer. SNMS is presented as a powerful tool for the characterization of element distribution and the interface quality of un-doped ZnO and Ga-doped ZnO thin films deposited by RF magnetron sputtering on Si wafers. The width of the interlayer between the ZnO film and the Si substrate was influenced by the attained depth resolution and by the thin film surface roughness. The quantitative analysis of the interface region revealed an increase of the concentration of the dopant element.

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Kinetics of sub-surface dislocation motion during the growth of magnetite thin films on Pt(111)

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Magnetite is a material well known for its scientific and technological application in heterogeneous catalysis, spin electronic devices and more [1]. Magnetite thin films incorporate often crystalline defects, such as dislocations and anti-phase domain boundaries (APBs), which are responsible for a very large magnetic saturation field, increase in resistivity and are preferential adsorption sites for molecules [2]. APBs in magnetite thin films have been extensively studied in the past [2-3], mainly with dark field transmission electron microscopy, which gives information about their bulk structure. Less is known about their surface termination and their kinetic behaviour during the thin film growth. In this poster, we show a study on linear defects ascribable as sub-surface dislocations present in Fe₃O₄(111) thin films grown on Pt(111) single crystal. The investigation of sub-surface dislocations in magnetite thin film is of great importance because they can prelude to the formation of APBs. For this purpose, we put particular focus on the preparation conditions in which they are formed, on their surface appearance and on their motion during the thin film growth. The experiment was performed with SMART, the energy-filtered, aberration-corrected Low Energy Electron Microscope and PhotoEmission Electron Microscope capable of real-time observation of the surface at different environmental conditions with a lateral resolution of a few nm [4]. The experimental data are also compared with theoretical LEEM simulation based on the Contrast Transfer Function approach [5], in order to gain information about the line defect morphology at the atomic level.

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The structure and phase composition of iron oxides on Pt(111)

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The (111) surface of magnetite single crystals as well as of epitaxial films can become very heterogeneous when the condition of their formation are far from the equilibrium [1, 2]. The observed inhomogeneities, termed in the literature as “biphase” [2], have a strong tendency to order in a quasi-hexagonal structure with a periodicity 3-6 nm. The character and depth of the surface changes associated with different observed biphasic superstructures is so far unclear.

We have studied the effect of reduction on the surface structure on magnetite Fe₃O₄(111) films. The stoichiometry of the magnetite films was modified by deposition of metallic iron, followed by the UHV annealing.

Magnetite films were grown on a Pt(111) single crystal by reactive Fe deposition in oxygen atmosphere and subsequent UHV annealing. The film surface structure was analyzed using LEED and STM, whereas the reliable method of the composition determination was the conversion electron Mössbauer spectroscopy (CEMS) applied *in situ* under UHV conditions. The stoichiometric Fe₃O₄(111)/Pt(111) films displayed electronic and magnetic properties (including the Verwey transition) characteristic for bulk magnetite down to the 1 nm thickness, except of the interfacial region, where an FeO layer was identified.

The addition of iron resulted in a modification of the surface structure from with the regular Fe₃O₄(111) termination to the bi-phase reconstruction [2]. Whereas the LEED pattern weakly depends on the amount of iron added, STM shows several biphasic structures that successively appear during reduction (annealing) under UHV condition. The CEMS spectra revealed that the phase composition of a 5 nm film, initially only weakly dependent on the Fe thickness, abruptly changes above 2 ML of iron.

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The structure of oxalic acid on Cu(110) and Cu(111)

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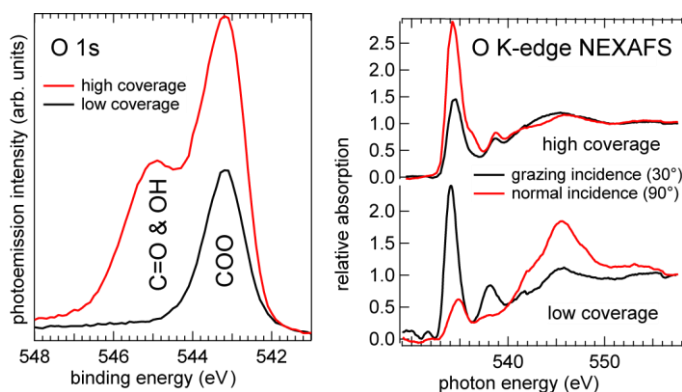
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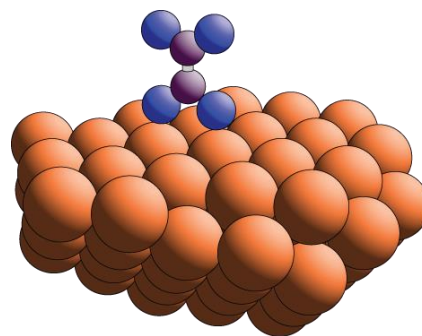
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The structure of oxalic acid (HOOC-COOH) on Cu(110) has been investigated experimentally by the combination of STM, LEED, UPS, SXPS, NEXAFS and scanned-energy mode photoelectron diffraction (PhD), while on Cu(111) oxalic acid adsorption has been studied by PhD and NIXSW. On both surfaces SXPS and NEXAFS indicate that at low coverage the adsorbed species is doubly-deprotonated, flat-lying OOC-COO, whilst at higher coverage an upright-standing singly-deprotonated OOC-COOH species is observed.



The figures show O 1s SXP spectra and O K-edge NEXAFS from the low and high coverage states. At low coverage only a single O 1s peak is seen, consistent with the fully deprotonated di-oxalate species. At higher coverage a second feature appears, consistent with the presence of both the deprotonated O atoms and the =O and -OH species of the acid. The angular dependence of the NEXAFS π -resonance at threshold clearly shows the two different molecular orientations.

O 1s PhD data from the standing-up phase on Cu(110) identify the structure as bidentate bonding to the surface, with O atoms close to atop sites and a Cu-O bondlength of 2.0 Å, in agreement with the previously-determined structure of other carboxylates on this surface including formate, acetate and benzoate. (Note that the H atom is not included in the figure as this weak scatterer is not included in the PhD calculations). O 1s PhD data indicate a similar local adsorption geometry for the standing-up phase on Cu(111). So far, however, multiple scattering simulations of the O 1s PhD from the lower-coverage phases have failed to identify an acceptable structural model based only on unreconstructed surfaces, and a range of alternative reconstruction models are now being investigated.



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Island Ripening via a Polymerization/Depolymerization Mechanism

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Island ripening is a fundamental process in chemistry in which the initially small particles of a new phase grow in size thus reducing interfacial energies. In Ostwald ripening an evaporation/condensation process causes the large particles to grow at the expense of smaller ones. Here we report on a ripening mechanism based upon a chemical reaction, which therefore requires reaction conditions in order to proceed [1]. In catalytic methanol oxidation on ultrathin (sub-monolayer quantities) supported vanadium oxide (VO_x) layers an extensive mass transport takes place, resulting in a reaction-controlled ripening. An initially homogenous 2D VO_x film on Rh(111) condenses during catalytic methanol oxidation into large circular VO_x islands (20 – 100 μm diameter). These islands undergo a dynamic redistribution process in which they move towards each other and coalesce. The island motion and coalescence are explained by a reversible depolymerization of the 2D-network structure of VO_x into small clusters that is controlled by the oxygen coverage [2]. Remarkably the VO_x redistribution is associated with a drastic increase of the catalytic activity. This can be seen in Fig. 1 by the sharp rise of formaldehyde production rate starting at 550 °C. We have studied the same catalyst system with the reactions O₂ + H₂, NH₃ + O₂ and CO + O₂ by applying the same reaction conditions. In all cases a similar behaviour was observed. The dynamic VO_x redistribution was studied with PEEM and SPELEEM, the VO_x surface structures were examined with LEED and the catalytic activity of the ultrathin VO_x layers was analyzed with QMS.

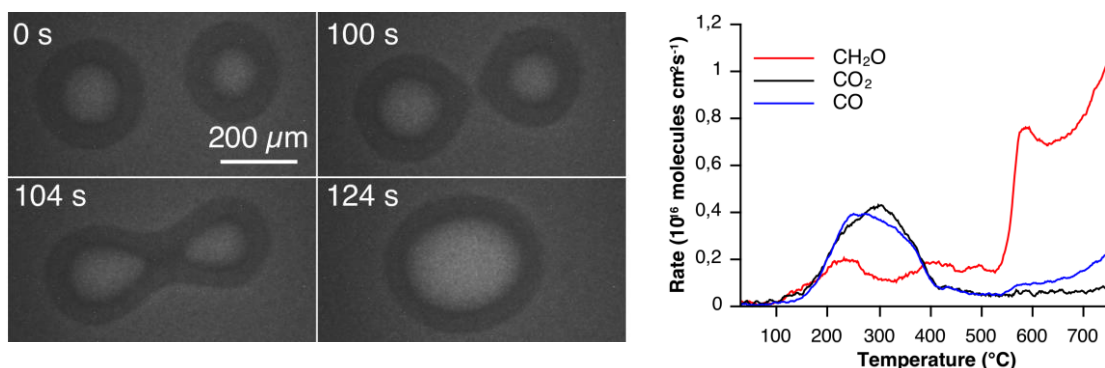


Figure 1: PEEM image sequence of the VO_x island coalescence during catalytic methanol oxidation (left) and production rate of the formed products carbon monoxide, carbon dioxide and formaldehyde (right).

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NFFA-EUROPE: An open access resource for experimental & theoretical science

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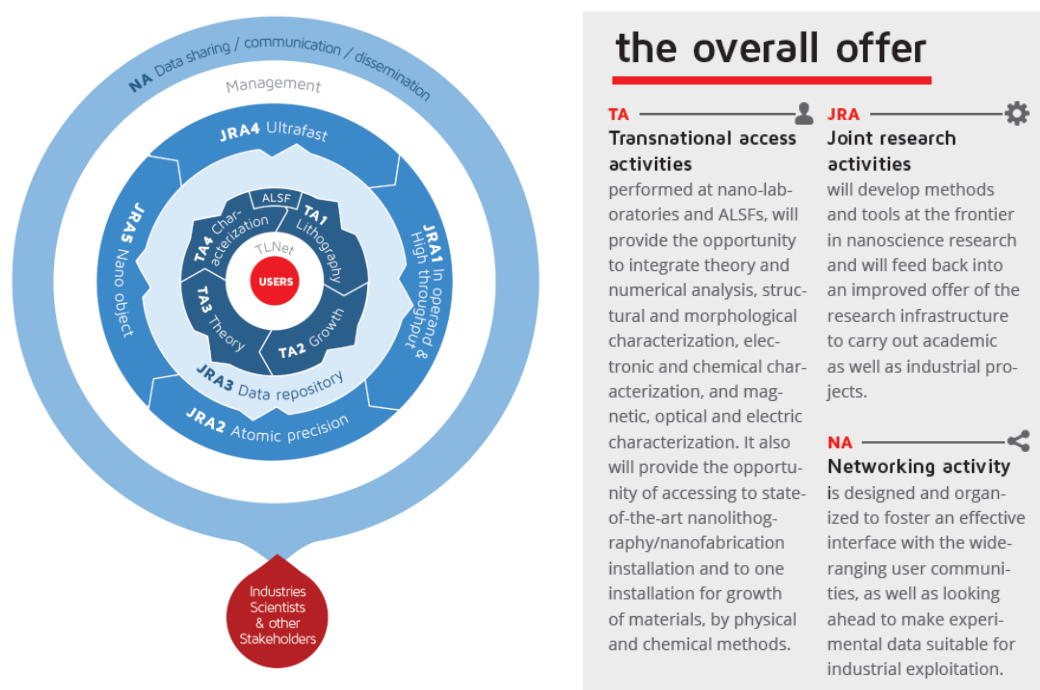


Figure 1: NFFA-Europe project activities and their relations (left) and description of the overall offer (right).

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CERIC-ERIC: One distributed facility for multi- technique experiments

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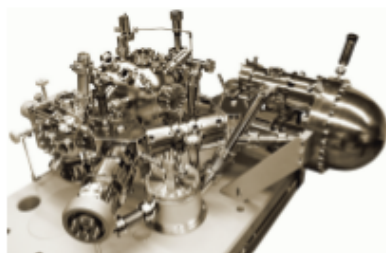
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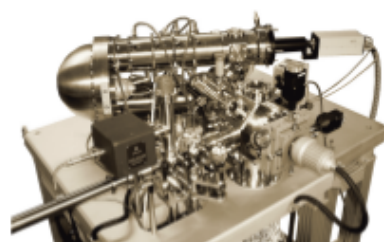
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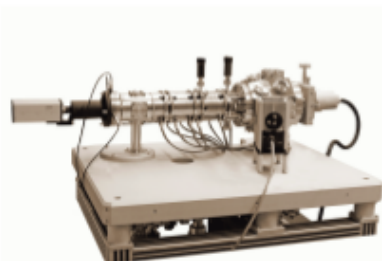


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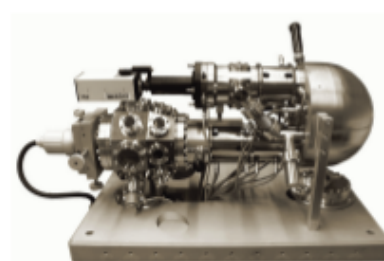
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PEEM III
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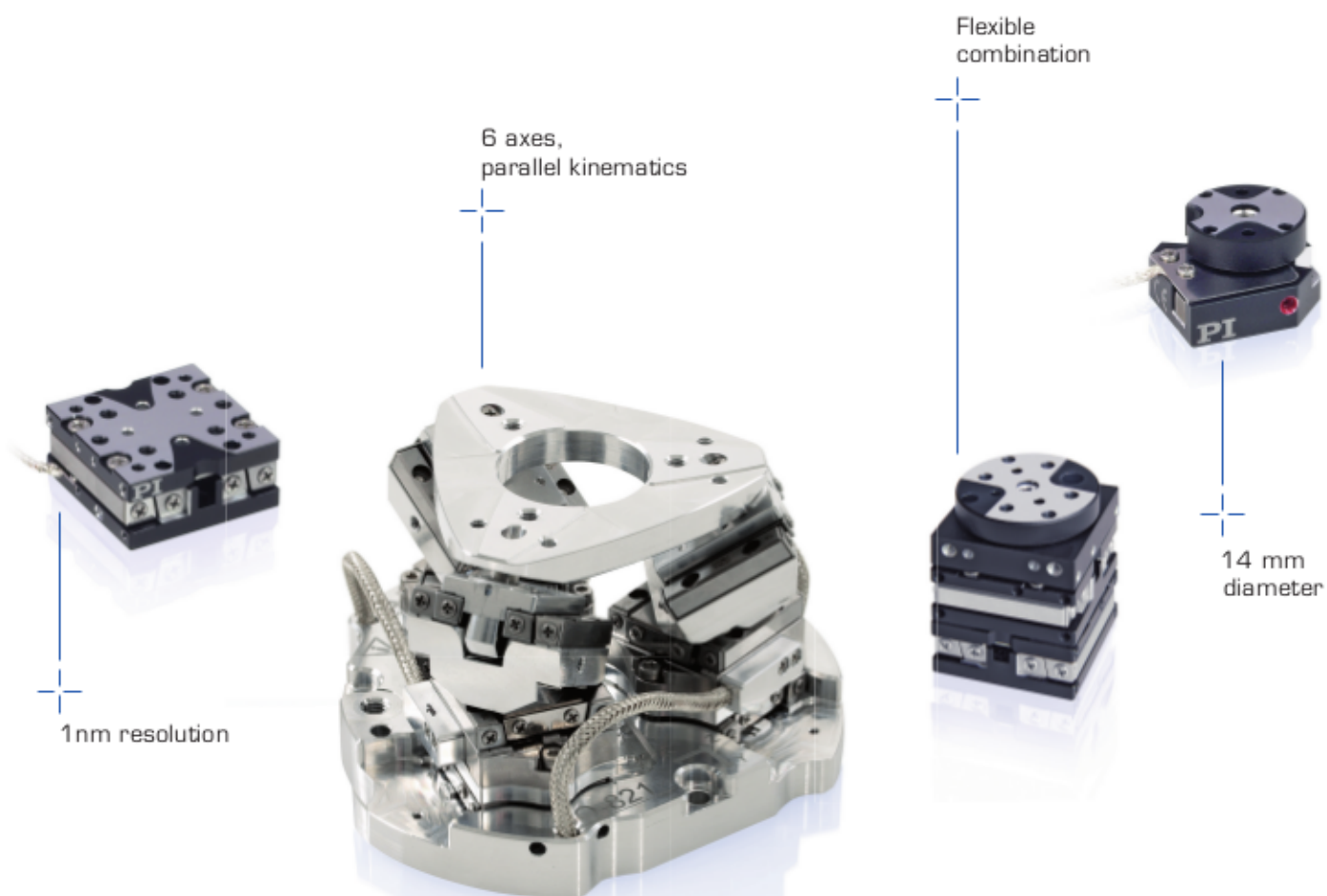
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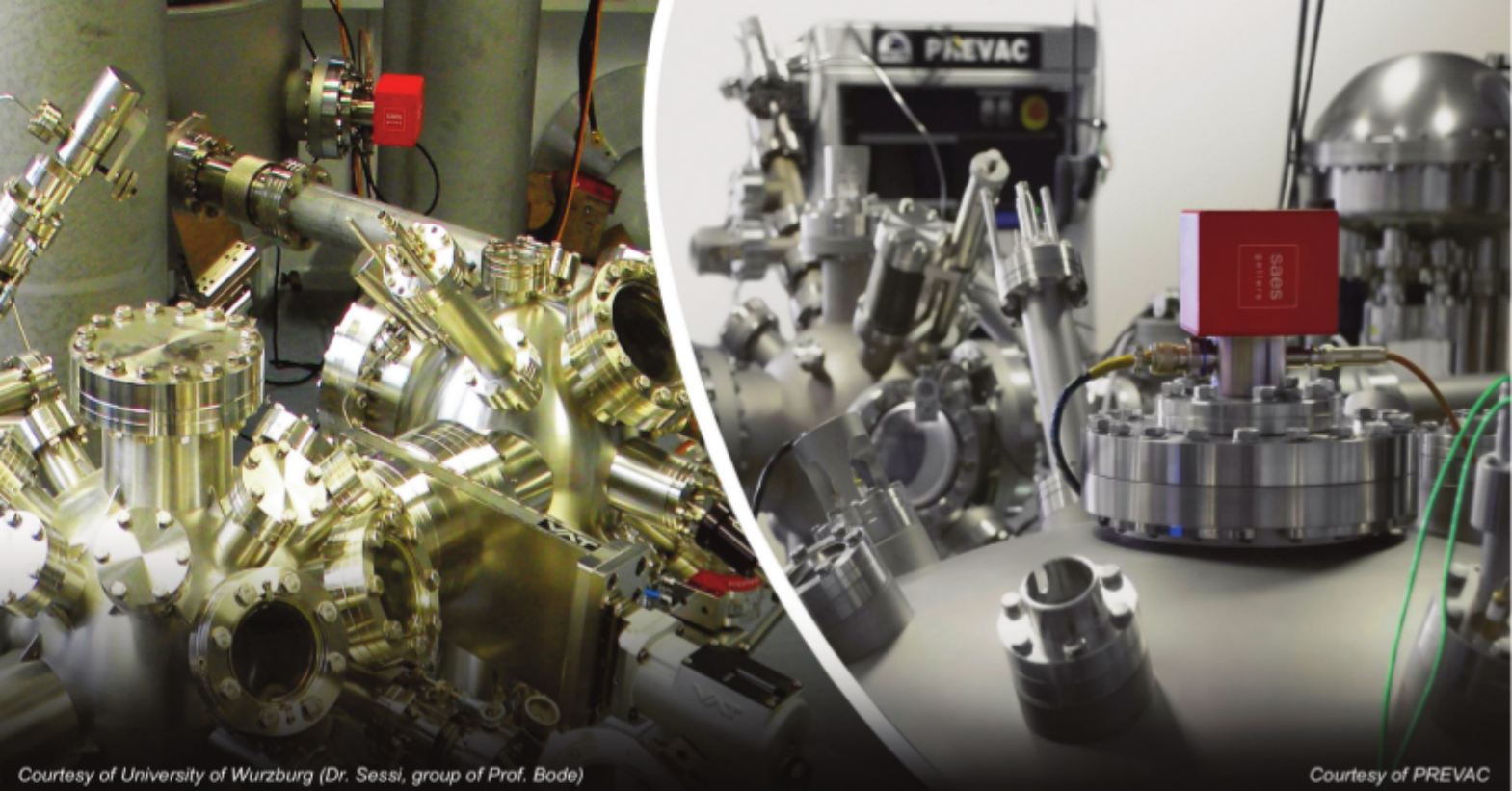
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