

O 87: Metal Substrates: Structure, Epitaxy and Growth

Time: Thursday 15:00–18:15

Location: S053

O 87.1 Thu 15:00 S053

Zn on Au(111) - growth and alloy formation — ●KONSTANTIN M. SCHÜTTLER and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Methanol is a promising molecule for chemical energy storage, e.g. by use of H₂ from regenerative sources. Industrially, methanol is synthesized from syngas (CO/H₂) over Cu/ZnO catalysts. The synthesis of “Green Methanol” from CO₂/H₂ as “solar fuel” could make this synthetic fuel even independent of fossil energy carriers. It has recently been demonstrated that under reaction conditions the ZnO support of Cu/ZnO catalysts is partly reduced to Zn, forming a CuZn alloy which is proposed to contain the active site for this reaction. For the hydrogenation of CO₂, Au/ZnO is a highly promising catalyst, and in analogy to Cu/ZnO, reduction of ZnO and formation of bimetallic AuZn surfaces under reaction conditions is plausible.

In order to gain more insight into the formation and nature of active sites, we started to study the formation, structure and chemical properties of bimetallic Zn/Au(111) surfaces as structurally well-defined 2D model catalysts. Here we present first UHV-STM measurements on the growth and (surface) alloy formation of Zn on Au(111). Nucleation and 2D growth of Zn islands seems to start both at the elbow sites of the Au(111) herringbone reconstruction and at step edges. Equally possible, however, is that the observed structures are created by place exchange of Au atoms into the first layer, which then act as trap sites for Zn and Au adatoms, where the latter result from Zn place exchange. This is tested in ongoing STM experiments.

O 87.2 Thu 15:15 S053

Structural analysis of Pd on W(110) — ●JEANNETTE KEMMER and MATTHIAS BODE — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

We report on a scanning tunneling microscopy (STM) study of the thin-film growth of Palladium (Pd) on W(110). Depending on the Pd thickness various surface superstructures are observed. Sub-monolayer Pd coverages exhibit periodic stripes running along the [001] direction of the substrate. Their periodicity amounts to (7.3 ± 0.5) nm and does not change significantly up to coverages of 0.88 atomic layers (AL). Additionally, zigzag lines appear in between the straight stripes. Atomically resolved images reveal that these stripes mark transition regions between inequivalent asymmetric Pd adsorption site, i.e. left- and right-shifted relative to the centro-symmetric hollow adsorption site usually found on bcc(110) surfaces. At Pd coverages between 0.93 AL to 1.01 AL the stripe anisotropy along the [001] direction of the substrate decrease. At the same time the stripe periodicity steeply increases, resulting in structural domain sizes up to 100 nm with right- and left-shifted adsorption sites. The second layer starts to grow on step edges and as hexagonal islands with additional stripes on top. The stripes are fully developed when the second layer is completely closed. Island growth starts with the third layer and marks the transition between the bcc crystal structure of the substrate and the fcc crystal structure of the Pd.

Invited Talk

O 87.3 Thu 15:30 S053

Heteroatom-doped Molecular Nanostructures on Surfaces — ●SABINE MAIER — Department of Physics, Friedrich-Alexander University Erlangen-Nürnberg, Germany

The interest in molecular nanostructures on surfaces emerges from their prospective applications in nanoscale electronics, solar cells, energy storage devices, and other fields. Non-covalent intermolecular interactions in self-assemblies facilitate the formation of long-range ordered patterns. In contrast, the on-surface synthesis of covalent molecular structures improves the stability and intermolecular charge transport at the expense of structural control owing to the irreversible nature of the newly formed covalent bonds, which prevents an error correction.

Here, we review recent high-resolution scanning probe microscopy experiments complemented by density functional theory on non-covalent and covalent molecular structures built from carefully designed functionalized triphenylamines. First, hierarchic formation principles of covalently-linked nanoporous networks through surface-assisted Ullmann coupling reactions are shown. Design rules to po-

tentially overcome the lack of long-range order in such networks will be discussed together with their electronic properties and host-guest chemistry. In the second part, electronically decoupled self-assemblies on bulk insulators are presented. We show how intermolecular and molecule-substrate interactions can be tuned by functional groups in order to achieve one-, two-, or three-dimensional assemblies in a controlled way.

O 87.4 Thu 16:00 S053

Atomic diffusion through vacancies as driving mechanism for structure formation of bimetallic surface alloys — ●LUIS MANCERA and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

The local catalytic activity of surface alloys is usually investigated using periodic DFT calculations, and the energetics of the surface structure is based on periodic arrangements. Still, real surface alloys are often far away from having regular atomic distributions. Furthermore, it is not clear whether the resulting structures are governed by thermodynamics, i.e., whether these structures correspond to a minimum of the free energy, or whether their arrangement is a consequence of kinetic hindering that does not allow the system to reach thermal equilibrium. Thus a generalized approach is necessary in order to understand the stability of surface alloys for different mixing ratios of the constituents. Therefore, we investigate the structure formation of surface alloys by generalizing the local description provided by periodic DFT into a kinetic Monte Carlo (kMC) approach that allows to address the temporal evolution of bimetallic structures. As self-diffusion in metals is usually mediated via vacancies, as a first step we concentrate on the determination of transition rates for vacancy diffusion processes taking variations in the local environment into account.

O 87.5 Thu 16:15 S053

The surface reconstruction of Pt(001) revisited — RENE HAMMER¹, OLIVER KRAHN¹, KLAUS MEINEL¹, and ●WOLF WIDDRA^{1,2} — ¹Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck Institut für Mikrostrukturphysik, Halle, Germany

The complex hexagonal reconstruction of the (001) surfaces of platinum and gold is under debate since decades [1,2]. In the present study, we combine SPA-LEED and STM together with LEED simulations based on a Moiré approach to address the Pt(001) reconstruction. Smooth samples annealed at 900°C show two domains of a $c(26 \times 128 \pm 10)$ superstructure. The superstructure evolves from a Moiré-like buckling of a quasi-hexagonal top layer (hex). The lattice vectors of the hex are reduced to 0.9606a and 0.9629a with respect to the interatomic distance a of Pt(001). The former runs exactly along [011] or [01 $\bar{1}$] whereas the latter one deviates by 120.08° from that directions. Sample annealing at 1000°C stimulates a continuous rotation of the hex where all angles between 0 and $\pm 0.8^\circ$ are simultaneously realized. At 1100°C, the hex resides in fixed rotation angles of $\pm(0.77^\circ \pm 0.01^\circ)$. Sputtering at elevated temperatures lowers the value n of the $c(26 \times 2n)$ superstructure down to 34 and leads to a continuous rotation in the range of $\pm 0.8^\circ$. In many aspects, the Pt(001) reconstruction displays a similar behavior as found for Au(001) [2].

[1] P. Havu et al., Phys. Rev. B 82 (2010) 161418(R) and references therein;

[2] R. Hammer et al. Phys. Rev. B 90 (2014) 035446.

O 87.6 Thu 16:30 S053

Mapping the contact formation of a gold tip approaching the Au(111) surface — ●LUKAS GERHARD¹ and WULF WULFHEKEL^{1,2} — ¹Institut für Nanotechnologie (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen — ²Physikalisches Institut (PI), Karlsruhe Institute of Technology (KIT), 76049 Karlsruhe

The understanding of the interplay between forces, relaxations, and electron transport during formation and breaking of a contact between two metallic electrodes is of fundamental interest for nano-scale electronics. Here we use the gold tip of a low-temperature scanning tunneling microscope (STM) to reproducibly form and break a contact with a reconstructed Au(111) surface without degradation of the electrodes. From a set of about 20.000 individual measurements we mapped the work function, the tip-sample separation at jump into contact, the

jump in conductance, and the hysteresis in the approach-retract curve with atomic resolution on an area of $1 \times 9 \text{ nm}^2$ spanning the $22 \times \sqrt{3}$ unit cell of the reconstruction. The variation of these parameters due to the difference in the local coordination environment is discussed.

O 87.7 Thu 16:45 S053

Epitaxial growth of tin(IV)-phthalocyanine-dichloride on Ag(111) — ●CHRISTIAN ZWICK¹, YUI IOKA², ROMAN FORKER¹, SATOSHI KERA^{2,3}, and TORSTEN FRITZ¹ — ¹Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — ²Graduate School of Advanced Integration Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 2638522, Japan — ³Institute for Molecular Science, Myodaiji, Okazaki 4448585, Japan

The peculiarities of the tetrahedron-like organic dye molecule tin(IV)-phthalocyanine-dichloride (SnCl_2Pc) originate from its functionalization with chlorine atoms above and below the central tin atom. These are expected to have a crucial impact on interface formation by virtue of their role as spacer groups and also due to the altered chemical reactivity compared to chlorine-free phthalocyanines. We report on the coverage-dependent growth of SnCl_2Pc on Ag(111). The thin films were characterized optically by in situ differential reflectance spectroscopy (DRS) and structurally by combined scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurements. Depending on the effective layer thickness we observe distinct phases of highly ordered flat-lying SnCl_2Pc molecules, leading to a bilayer structure as a precursor for a bulk-like crystal growth. For each of the subsequently observed structural phases, distinct optical properties can be assigned, allowing to qualitatively judge possible interactions with the surface and between stacked molecular layers in addition to the characterization of the structural reordering processes.

O 87.8 Thu 17:00 S053

On the adsorption behavior of a porphyrin on different Cu surfaces: A comparative scanning tunneling microscopy study — ●MICHAEL LEPPER, LIANG ZHANG, MICHAEL STARK, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen

Self-assembly of functional molecular building blocks on well-defined surfaces is a promising approach for the bottom-up fabrication of two-dimensional nanostructures with outstanding properties. In this respect, porphyrins are particularly attractive due to their distinct chemical and physical properties. In this study, we compare the adsorption of 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) on different substrates, i.e., Cu(110) and Cu(110)-(2x1)O, under ultra-high vacuum conditions by scanning tunneling microscopy. At room temperature, supramolecular arrangements are observed for 2HTTBPP on Cu(110)-(2x1)O, while on Cu(110) individual molecules in a disordered layer are found. Interestingly, the intramolecular conformations on the two substrates are quite different. The corresponding findings are interpreted by accounting for specific molecule-molecule and molecule-substrate interactions. In addition, the so-called self-metalation of 2HTTBPP with Cu atoms will be reported and discussed. Supported by the DFG through FOR 1878 (funCOS) and the AvH Stiftung.

O 87.9 Thu 17:15 S053

From Porphyrins to Pyrphyrins: Adsorption and Metalation on Au(111) — ●GERSON METTE¹, DENYS SUTTER¹, YELIZ GURDAL², STEPHAN SCHNIDRIG², BENJAMIN PROBST², MARCELLA IANNUZZI², JÜRIG HUTTER², ROGER ALBERTO², and JÜRIG OSTERWALDER¹ — ¹Physik-Institut, Universität Zürich, CH-8057 Zürich — ²Institut für Chemie, Universität Zürich, CH-8057 Zürich

Pyrphyrin, a tetradentate bipyridine based macrocycle, represents an interesting but widely unexplored molecular ligand. It shares some similarities with the far better known porphyrins, but it is constituted by pyridyl subunits instead of pyrroles. A high stability of pyrphyrin and its corresponding complexes is suggested. Metal complexes based on pyrphyrin ligands have recently shown promise as water reduction catalysts in homogeneous photochemical water splitting reactions [1].

In this study, we examined the adsorption and metalation of pyrphyrin on a single crystalline surface by means of low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), x-ray pho-

toelectron spectroscopy (XPS) and density functional theory (DFT). Pyrphyrin coverages of approximately one monolayer and less were obtained by sublimation of the molecules on a Au(111) surface at room-temperature. Cobalt deposition and subsequent annealing led to the formation of Co-ligated pyrphyrin molecules. An intermediate state of the metalation reaction was observed and the reaction steps for the Co metalation of pyrphyrin molecules on Au(111) were established.

[1] E. Joliat et al., (in preparation).

O 87.10 Thu 17:30 S053

Structure and morphology of sulfur-terminated Si(111) — ●LARS BUSS, THOMAS SCHMIDT, and JENS FALTA — Universität Bremen, Bremen, Germany

The preparation of sulfur-terminated Si(111)-surfaces aims at the functionalization and passivation of the surface as a template for the growth of layered materials thin films, as the sulfur-termination prevents strong chemical bonding between the substrate and the adsorbate. Therefore the surface-reconstruction and the morphology of the sulfur-terminated Si(111)-surface have been examined with both SPA-LEED and STM. In a small temperature range, a phase transition from (7×7) to a reconstruction, previously reported as (4×4) by Metzner et al. (Surf. Sci. **377** (1997) 71), was found. Our analysis, however, reveals that this reconstruction is actually a $(\frac{2}{1} \frac{0}{2})$ -reconstruction, which occurs in three rotational domains on the surface. Furthermore we observe that the surface is etched upon prolonged exposure to the sulfur-flux.

O 87.11 Thu 17:45 S053

Decay of isolated Hills and Saddles on Si(001) studied by LEEM — ●PIERRE KIRSCHBAUM¹, LOTHAR BRENDL¹, KELLY R. ROOS², MICHAEL HORN-VON HOEGEN¹, and FRANK-J. MEYER ZU HERINGDORF¹ — ¹Faculty of Physics and Center of Nanointegration (CeNIDE), University of Duisburg-Essen, Lotharstraße 1, 47057 Duisburg — ²Present Address: Faculty of Engineering and Physics, Bradley University, Preoria, IL 61625

Dark field low energy electron microscopy is used to study the high temperature decay of isolated hills and saddle points on Si(001). We find different temperature dependent decay rates for the top of the hill compared to a saddle point with low step density that is present in the vicinity of the hill. The decay rate of the hill is always higher than the decay rate at the saddle. The two rates converge with increasing temperature and become equal at temperatures above 1060°C. We also report an alternating fast and slow decay rate for the layer-by-layer decay of the hills. This surprising finding is independent of temperature and is explained by macroscopic strain in the sample. In-situ deposition of Au on the Si(001) surface increases the decay rates of the hill and saddle by more than a factor of ten.

O 87.12 Thu 18:00 S053

Growth, morphology, and stoichiometry of cobalt germanide islands on Ge(001) — ●MORITZ EWERT¹, THOMAS SCHMIDT¹, INGA HEIDMANN¹, JAN INGO FLEGE¹, TOMASZ GRZELA², MICHAEL FOERSTER³, LUCIA ABALLE³, THOMAS SCHROEDER², and JENS FALTA¹ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²Leibniz Institute for Innovative Microelectronics (IHP), Frankfurt (Oder), Germany — ³ALBA CELLS, Barcelona, Spain

In today's silicon technology, the integration of germanium structures is one of the most promising routes to improve the performance of CMOS devices. One of the challenges is the fabrication of low-resistance metal/Ge contacts. As metallization contact materials, Co germanides and Ni germanides are regarded to have the best perspective.

We have investigated the growth of Co germanide on Ge(001) by Co metal deposition using low-energy electron microscopy and microdiffraction as well as x-ray absorption photoemission microscopy (XAS). Both for room temperature (RT) deposition followed by thermal annealing as well as for metal deposition at elevated temperatures, we observe the formation of Co germanide 3D islands. Extremely anisotropic, needle-like 3D islands extending in $\{110\}$ directions coexist with rather compact ones. XAS measurements at the Co L absorption edge show that for deposition at room temperature, metallic Co is present on the surface that reacts with the Ge during subsequent thermal annealing. The Co germanide forms 3D Volmer-Weber islands. Interestingly, local XAS reveals that different island morphologies are related to different germanide stoichiometries.