O 49: Surface chemical reactions I

Time: Wednesday 10:30–12:45 Location: H42

O 49.1 Wed 10:30 H42

Temperature programmed desorption from surfaces of electronic devices — Andreas Peckhaus, Kevin Stella, •Detlef Diesing, and Eckart Hasselbrink — Institut für Physikalische Chemie, Universität Duisburg Essen

Surface chemical reactions depend crucially on the cleanliness and morphology of the surface. Usual cleaning procedures as sputtering and annealing can be well applied to single crystal surfaces. But thin film electronic devices can be hardly exposed to such kind of procedures since either the thermal stability of the devices is too low or the devices internal interfaces may be damaged be sputtering ions. We present first experiments on temperature programmed desorption of CO on the platinum surface of thin film platinum-silicon oxide-(n-type)-silicon devices. Problems as damages in the platinum films due to electromigration and degradation of the oxide films in the high temperature range > 600 K are discussed. We show that heating rates up to 3 K/s from 150 K to 600 K can be established with reproducible desorption peaks indicating an activation energy of desorption of 90 - 120 kJ/mol for CO adsorbed on the device surface.

O 49.2 Wed 10:45 H42

Functionalization of AlGaN/GaN heterostructures with TFAAD — •Stefan Udo Schwarz[1], Volker Cimalla[2], Christoph Nebel[2], and Oliver Ambacher[2] — [1]Institute of Microsystem Technology (IMTEK), University of Freiburg, Georges-Köhler-Allee 106, 79110 Freiburg, Germany — [2]Fraunhofer Institute for Applied Solid State Physics, Tullastraße 72, 79108 Freiburg, Germany

AlGaN/GaN high electron mobility transistors (HEMTs) show great promise for the realization of sensors for biomolecular, pharmaceutical and medical purposes. The high sensitivity and the stability in biological solutions are great advantages of this principle. The transduction is based on the AlGaN/GaN heterostructure. Charges on its surface influence the electron density in the 2-dimensional electron gas (2DEG) near the interface of the heterostructure. For a specific sensor, biological recognition methods shall be used. Therefore biomolecules need to be covalently linked to the semiconductor. The surface must be functionalized with a single layer of molecules that form covalent bonds to the surface and present functional groups for the connection with the biomolecule. In this work we investigate the functionalization of AlGaN/GaN heterostructures with 10-Trifluoroacetamiddec-1-ene (TFAAD), a molecule that can bond to GaN in a photochemical reaction and has a protected Amino group for the further procedure. The focus is on the influence of the illumination spectrum and surface pretreatments on the reaction kinetics and the resulting layer morphology with respect to the designated application.

O 49.3 Wed 11:00 H42

Adsorption and thermal behaviour of ethane and ethene on oxygen precovered Ni(111) — •Michael Peter Andreas Lorenz[1], Thomas Fuhrmann[1], Karin Gotterbarm[1], Regine Streber[1], Fabian Bebensee[1], Christian Papp[1], Reinhard Denecke[2], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — [2]Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig

Ni as well as NiO are widely-used catalysts in chemical industry. To understand the adsorption and reaction properties of small hydrocarbons on such surfaces we studied ethane and ethene on clean and oxygen precovered Ni(111) by means of XPS using synchrotron radiation at BESSY II. The gases were dosed using a supersonic molecular beam; for C_2H_6 this provided the kinetic energy required for the activated adsorption yielding adsorbed C_2H_5. On clean Ni(111) both C_2H_5 and C_2H_4 give rise to two separate C 1s peaks, indicative of a different local environment for the two C atoms in both cases. In contrast, on oxygen precovered Ni(111) only one C 1s peak is observed after exposing the surface to C_2H_4, and for C_2H_5 the peak separation is strongly reduced, indicating major changes in the adsorption geometries. Furthermore, we also studied the thermal evolution of the adsorbed hydrocarbons and found significant differences between oxygen free and oxygen precovered Ni(111).

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O 49.4 Wed 11:15 H42

Switching Single Azopyridine Supramolecules in Ordered Array on Au(111) — •Yongfeng Wang[1], Xin Ge[1], Guillaume Schull[1], Richard Berndt[1], Hao Tang[2], Claudia Bornholdt[3], Felix Koehler[3], and Rainer Herges[3] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel, Germany — [2]CEMES/CNRS, France — [3]Institut für Organische Chemie, Christian-Albrechts-Universität, D-24098 Kiel, Germany

Understanding and controlling molecular switches on surfaces is of interest in both fundamental science and functional device at the single molecule level. Single molecular switches have been realized by modifying covalent bonds or ionic bonds. Decoupling of the reactive component of the molecule from a metal substrate by an insulating layer can be necessary as reversible switching is usually quenched on metals for the rather high barrier to overcome and the short lifetime of excitations. In contrast to molecules, supramolecules are connected through weak noncovalent interactions like hydrogen bonding. Lower energy barriers to switching may be expected for these weaker bonds. Here we report on supramolecular switches of 4,4-azopyridine trimers and 4-phenylazopyridine dimers in ordered array on Au(111). During switching, a single weak C-H...N hydrogen bond breaks and reforms. For 4,4-azopyridine, the switching mechanism occurs via electron attachment. 4-phenylazopyridine dimer, however, can be switched by electric fields, too. Funding by the Deutsche Forschungsgemeinschaft through SFB 677 is acknowledged.

O 49.5 Wed 11:30 H42

Atomistic modelling of the oxidation of Co, Cr and CoCr alloy surfaces — •Janina Zimmermann[1,2] and Lucio Colombi Ciacchi[2,3] — [1]Fraunhofer IWM, Freiburg, Deutschland — [2]Fachbereich Produktionstechnik, Universität Bremen, Deutschland — [3]Fraunhofer IFAM, Bremen, Deutschland

In this work, first-principles molecular dynamics based on density-functional theory is employed to investigate the early oxidation stages of the Co(0001), Cr(110) and CoCr(0001) surfaces. Oxide nucleation on cobalt follows a metastable path, with the place-exchange of metal and oxygen atoms leading to the growth of an open, pseudo-amorphous oxide structure with evident Co_3O_4-like features. Instead, the oxidation of Cr(110) occurs along an energy path close to thermodynamic equilibrium and limited by Cr-ion diffusion already in the earliest oxidation stages. The initial formation of highly oxidized chromate-like structures seems to be precursory for the subsequent growth of Cr_2O_3 thin films. The oxidation of CoCr alloys occurs via selective oxidation of chromium, which leads to vacancy formation and enables the diffusion of oxygen atoms into inner atomic layers. The outward diffusion of chromium is strongly facilitated by the matrix of amorphous cobalt oxide. These results suggest that superficial oxidation may proceed along two distinct possible pathways: a thermodynamically stable path along the potential energy minimum surface and a metastable, kinetically driven path that results from the high heat release during the dissociation of O_2.

O 49.6 Wed 11:45 H42

'QM/Me' - a novel embedding approach for adsorbate dynamics on metal surfaces — •Jörg Meyer[1] and Karsten Reuter[1,2] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin (Germany) — [2]Technische Universität München (Germany)

The dissociative adsorption of oxygen molecules on metal surfaces is a commonly known, highly exothermic reaction and in its slow or fast form of great importance for corrosion or oxidation catalysis, respectively. However, knowledge about atomistic details of the heat dissipation, a central conceptual concern, is very limited at best. Even on the level of Born-Oppenheimer potential energy surfaces, accurate dynamical *ab-initio* descriptions of such reactions are quite challenging from a computational point of view: Modeling the excitations of substrate phonons within periodic boundary conditions requires huge supercells, whereas traditional 'QM/MM' embedding schemes do demand unfeasibly large metal clusters. In the novel 'QM/Me' approach presented here, the adsorbate-substrate interaction is obtained from periodic first-principles calculations in convenient supercells and combined with the description of a 'bath-like' substrate based on classical potentials, which are parametrized to seamlessly fit the first-principles data. We apply our approach to dissociative adsorption of O_2 and H_2 on Pd(100) using density-functional theory and a modified embedded atom potential. In both cases, we observe a dominant fraction of the released chemisorption energy to be dissipated into the bulk already on a femtosecond time scale. Implications for the adsorbate dynamics will be discussed.

O 49.7 Wed 12:00 H42

Material and Orientation dependent activity for heterogeneously catalyzed carbon-bromine bond homolysis — •Hermann Walch, Rico Gutzler, Thomas Sirtl, Georg Eder, and Markus Lackinger — LMU Munich, Section Crystallography

Adsorption of the organic molecule 1,3,5-tris(4-bromophenyl)benzene on different metallic substrates, namely Cu(111), Ag(111) and Ag(110) has been studied by variable temperature Scanning Tunneling Microscopy (STM). Depending on substrate temperature, material and orientation, we observe a surface-catalyzed dehalogenation reaction. Deposition onto the catalytically active substrates Cu(111) and Ag(110) held at room temperature leads to cleavage of the carbon-bromine bonds and subsequent formation of protopolymers, i.e radical metal coordination complexes. However upon deposition on Ag(111) no such reaction has been observed. Instead, various self-assembled ordered structures based on intact molecules could be identified. Also sublimation onto either substrate held at 80 K did not result in any dehalogenation, thereby exemplifying that the dehalogenation reaction is thermally activated. We explain the differences in catalytic activity by charge transfer into unoccupied molecular orbitals and subsequent destabilization of the C-Br bond, whereby enhanced molecule-substrate interaction leads to an increasing magnitude of charge transfer. The interaction strength follows the general reactivity order Cu $>$ Ag $>$ Au for (111) faces and is generally enhanced on higher corrugated surfaces as the (110) facet in case of fcc substrates.

O 49.8 Wed 12:15 H42

High pressure behavior of Au/TiO$_x$/Pt(111) model catalysts — Luca Artiglia[1], Gaetano Granozzi[1], •Heinrich Hartmann[2], Thomas Diemant[2], Joachim Bansmann[2], and R. Jürgen Behm[2] — [1]Department of Chemical Sciences, via Marzolo 1, University of Padova, Italy — [2]Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

In an effort to bridge the pressure gap between model and realistic catalytic processes, three different ultrathin TiO_x on Pt(111) films have been prepared and investigated in-situ using XPS, LEED and IRAS to determine their stability in pure CO and CO/O_2 (1:1) at pressures up to 100 mbar. Two of the TiO_x films consist of reduced phases with and without a long range order of defects, the third film is a fully oxidized TiO_2 phase.

All three TiO_x phases were stable in a reducing CO atmosphere at RT. In a CO/O_2 (1:1) mixture, only the fully oxidized phase showed no structural and electronic changes. The reduced phases underwent a process of oxidative surface restructuring with a partial dewetting of the Pt(111) substrate.

The TiO_x/Pt(111) films were used as substrates to deposit Au nanoparticles (1-6 nm) with surface morphologies particular to each TiO_x phase. IRAS measurements on these Au/TiO_x/Pt(111) model catalysts showed, that the size of the Au nanoparticles (itself dependent on the morphology of the underlying TiO_x phase) plays a major role for the adsorption of CO, while the oxidation state of the oxide support is less relevant.

O 49.9 Wed 12:30 H42

Adsorption and reaction of SO_2 on clean and oxygen precovered Pt surfaces — •Regine Streber[1], Christian Papp[1], Michael Peter Andreas Lorenz[1], Andreas Bayer[1], Oliver Höfert[1], Wei Zhao[1], Sandra Wickert[2], Erik Darlatt[2], Reinhard Denecke[2], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — [2]Willhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig

Sulfur and its oxides are well-known poisons in large scale applications of heterogeneously catalyzed reactions. We studied the adsorption and thermal evolution of SO_2 on clean and oxygen precovered Pt surfaces by in-situ high-resolution XPS applying synchrotron radiation at BESSY II. The comparison of spectra obtained on flat and stepped Platinum allows to elucidate the role of steps for the thermal stability of different SO_2 species, and in particular for their disproportionation to S and SO_3 upon heating. On the oxygen precovered surfaces a fraction of SO_2 reacts to SO_3 immediately upon adsorption, even at temperatures as low as 100 K. Heating of the resulting mixed adsorbate layers first results in the reaction of all remaining SO_2 species to SO_3, followed by subsequent oxidation to SO_4 above 300 K.