A two-step mechanism for the oxidation of vacancies in graphene — Johan M. Carlsson, Felix Hanke, and Matthias Scheffpp — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

Complete oxidation of graphitic carbon materials leads to combustion and the formation of CO₂, but it has been suggested that partial oxidation of vacancies on the basal plane can yield catalytically interesting materials. The characterization of such oxidized graphite in temperature-programmed desorption (TPD) experiments detected a surprising amount of CO and significantly less CO₂ [1]. This work aims to clarify the oxidation mechanisms and surface structures under different experimental conditions. We use density functional calculations with PBE exchange correlation to obtain the structural and energetic properties of oxidized graphene vacancies. To understand the TPD spectra, reaction barriers and rates for CO and CO₂ desorption are calculated from transition state theory and the nudged elastic band method. An ab initio thermodynamics analysis indicates a significant partial pressure-dependence of the oxygen content in vacancies. This indicates a two step mechanism for the initial oxidation, by which strongly bound CO-releasing C-O-C and C=O groups saturate the vacancies under the ultra-high vacuum conditions of TPD experiments. Atmospheric partial pressures lead to additional oxygen adsorption into extended groups such as C-O-C-O and C-O-C=C, which in return can desorb as CO₂. [1] B. Marchon et al., Carbon 26, 507 (1988).

Structure and Composition of the TiO₂(110) Surface: From UHV to Realistic Reaction Conditions — Prok Kowalski, Bernd Meyer, and Dominik Marx — Lehrstuhl für Theoretische Chemie, Ruhr-Universität, D-44780 Bochum, Germany

Using DFT-based ab initio calculations in combination with a thermodynamic formalism we have calculated the relative stability of various structural models of the nonpolar, mixed-terminated TiO₂(110) surface in contact with a surrounding gas phase at finite temperature and pressure. Adsorption and desorption of hydrogen atoms and water molecules, as well as the formation of O vacancies were considered. Assuming thermodynamic equilibrium between the TiO₂ surface and an oxygen, hydrogen and water containing atmosphere, we constructed a phase diagram of the lowest free energy surface structures.

For a wide range of temperatures and pressures we find that water will be adsorbed at the surface. At full monolayer coverage, a molecular adsorption of water is preferential. The most stable adsorption site for hydrogen atoms is on-top of the bridging O atoms. Surprisingly, we find that in thermodynamic equilibrium the bridging O atoms can not be fully saturated which hydrogen, but only a maximum coverage of about 0.6 monolayer can be reached. The formation energy for O vacancies is found to be rather high so that O defects should only form at extremely oxygen poor conditions.

Dissociation of oxygen on Ag(100) by electron induced manipulation — Carsten Spodewig, Michael Mehlhorn, and Karina Morgensen — Institut für Festkörperphysik, Abteilung Oberflächen, Leibniz Universität Hannover, Appelstr. 2, 30167 Hannover, Germany

Low-temperature scanning tunneling microscopy is used to study oxygen dissociation on Ag(100). Deposition of oxygen on Ag(100) at 80K leads to small clusters of 1 to 10 molecules. Inelastic electron tunneling manipulation is used for the manipulation of these molecules. Thereby the STM tip is set above them, the feedback loop of the STM is switched off and a voltage is applied between tip and sample for exciting the electronic states of the molecules. For small energies (1500meV with 0.3 nA) the cluster roeiders, while above a distinct energy threshold the electron induced manipulation leads to a dissociation of the single molecules within the cluster. After manipulation in some cases dissociated pairs at different distances are found. However mostly only one atom of the dissociated molecule is observed. During the dissociation the tunneling current rises until a plateau of 5nA (3500mV) and remains there for some milliseconds. One possible explanation is a vertical orientation of the molecules as a metastable state before dissociating. In addition atomic resolution and a dissociated cluster during the same scan let us identify the adsorbate places of the dissociated atoms.
troscopy and Kelvin probe measurements were used to compare the evolution of the chemicurrents to the oxygen uptake of the samples.

Particle size dependence of adsorption state and photodesorption of NO on AgNPs on thin alumina film — Daniel Melugnetz, Ki Hyun Kim, Kazuo Watanebe, Dietrich Menzel, and Hans-Joachim Freund — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — Physik-Department E20, Technische Universität München, 85747 Garching

We report on the particle size dependence of adsorption state and photodesorption (PD) of NO adsorbed on Ag nanoparticles (AgNPs) with average diameter (d) between 2.5 and 12 nm, by using temperature-programmed desorption (TPD) and mass selected time-of-flight (MS-TOF) measurements. NO adsorbed at 75 K forms dimers which partly desorb and partly dissociate to form 2NO and N2O+O+ when heated. In TPD of NO shifts to higher peak temperature are found with increasing d. The PD cross section of NO at 2.3 and 4.7 eV in p-polarization increases monotonously when the particle size is reduced (~2 times for d=2.5 nm). At 3.5 eV in p-polarization, the PD cross section of NO increases rapidly as d decreases up to d=5 nm (~9 times) and then decreases as d is further reduced. At 2.3 and 3.5 eV the translational temperature of photodesorbing NO (Tt=700 K) does not change significantly with varying d. This indicates that the plasmon does not change the desorption dynamics of NO. However, at 4.7 eV a dramatic increase of Tt (up to ~1250 K) is observed for very small d (≤ 5 nm). We interpret these changes in terms of the size dependences of adsorption energy, plasmon strength, decay paths, and confinement.

Chemicurrent studies on bimetallic surfaces — Beate Schindler, Eckart Hasselbrink, and Detlef Diesing — Fachbereich Chemie und Centre for Nanointegration (CeNIDE), Universität Duisburg-Essen, D-45117 Essen, Germany

Chemical reactions on metal surfaces like adsorption and desorption reactions may dissipate their excess energy to substrate and adsorbate vibrations or to electronic degrees of freedom. This means excitation of e-h pairs directly at the surface. If the energy of the excited electrons is larger than the metal work function, the excess energy could be measured by light emission. Electronic surface excitations with smaller energies can be detected as internal currents in thin film tunnel or Schottky devices. We use tantalum–tantalum oxide–top metal tunnel junctions. As top metal 5 nm thick Pt films or 12 nm thick Au films were used. Both enable a ballistic transport of excited electrons (holes) with excess energies up to 1 eV from the surface to the oxide interface. The excited carriers are then detected in the tantalum backelectrode as a tunnel current. We compare the tunnel current traces induced by bunches of hydrogen atoms (5·10^{15} atoms in 20 sec) on the Au and Pt surfaces. For weak chemisorption systems constant chemicurrents are typical, which scale linearly with the atom flux JH. For strong chemisorption systems like Pt-H exponentially decaying chemicurrent traces (e^{-\alpha t}) are typical. Evaporating Au on top of Pt one can monitor the change of the chemicurrent trace from an exponentially decreasing type to a constant current type. This clearly shows that the adsorbate-surface chemistry determines the e-h pair excitation.

Investigating the binding sites of solvated electrons in polar layers adsorbed on Cu(111) — Michael Meyer, Julia Stähler, Uwe Bovensiepen, and Martin Wolf — Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Electron solvation is a well known phenomena in polar environments like NH3 and D2O, i.e., the localization and energetic stabilization of an excess electron due to the reorientation of the surrounding molecules. The properties and dynamics of solvated electrons constitute an active field of research. Here we present a surface science approach to determine the solvation site of excess electrons at the interface between polar molecular layers and a metallic substrate. We investigate the localization of excess electrons in amorphous D2O clusters and layers as well as amorphous ammonia layers, which are condensed on a Cu(111) substrate. Using two-photon photoemission spectroscopy(2PPE) we excite and probe excess electrons by UV and VIS laser pulses, respectively. For surface bound electrons adsorption of Xe leads to a change in binding energy due to a change of the dielectric environment which is directly measured by 2PPE. A transition from bulk bound solvated electrons to surface bound ones is found to occur at coverages of ~ 3 molecular layers where the continuous ice layers break up into laterally separated ice clusters. Remarkably the excess electrons in NH3-layers are always bound on the surface for the investigated thickness range of 2 to 22 layers. Possible scenarios regarding injection and detection probabilities as well as site configurations will be discussed.

Electronic valence band structure of V2O5 — Torsten Steimmel, Maximilian Kaulert, Helmut Dwekl, and Recardo Manzke — Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin

We will present high-resolution ARPES measurements of V2O5 single crystals carried out with He I resonance lamp and synchrotron radiation. The obtained experimentally band structure will be compared with calculations, e.g.[1] and [2]. By varying the excitation energy we have utilized the ARPES techniques to study also the time and photon flux dependence of valence band changes. This problem of degradation of the surface due to the high reactivity will be discussed referring to the previous experimental work, e.g. [3] and [4].


STM-induced Switching of Hydrogen on a Silicon(100) Surface: An Open-System Density Matrix Study — Karl Zenichowski, Tilman Klamroth, and Peter Saalfrank — Theoretical Chemistry, Institute of Chemistry, University of Potsdam, Germany

STM (scanning tunneling microscope) techniques offer the possibility to reversibly switch a hydrogen atom between two stable conformations on a silicon(100) surface dimer at room temperature [1].

We study the switching dynamics of a hydrogen atom, using an open-system density matrix formalism. The Liouvillian of Neumann equation in Lindblad form [2] is solved. Vibrational upward rates are calculated within the framework of first order perturbation theory, including expressions for resonant scattering and dipole coupling with tunneling electrons [3,4]. Vibrational deexcitation is treated by applying harmonic selection rules and scaling laws. Temperature is included via the principle of detailed balance.

The switching process in the high current regime is found to be governed by vibrational "ladder climbing" and subsequent tunneling in the electronic ground state. The influence of current, bias voltage, isotope mass, electric field, and dissipation strength is examined [5].