O 93: Surface Chemical Reactions

Time: Friday 10:15–13:00   Location: MA 043

O 93.1 Fri 10:15 MA 043

A two-step mechanism for the oxidation of vacancies in graphene — •JOHAN M. CARLSSON, FELIX HANKE, and MATTHIAS SCHEFFLER — 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 CO_2, 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 CO_2 [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 CO_2 desorption are calculated from transition state theory and the nudged elastic band method. An *ab-initio* thermodynamics analysis shows 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 O=C-O-C=O, which in return can desorb as CO_2. [1] B. Marchon *et al.*, Carbon **26**, 507 (1988).

O 93.2 Fri 10:30 MA 043

Structure and Composition of the $TiO_2(110)$ Surface: From UHV to Realistic Reaction Conditions — •PIOTR KOWALSKI, BERND MEYER, and DOMINIK MARX — Lehrstuhl fuer Theoretische Chemie, Ruhr-Universitaet, 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 $TiO_2(110)$ 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 TiO_2 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 extreme oxygen poor conditions.

O 93.3 Fri 10:45 MA 043

Dissociation of oxygen on Ag(100) by electron induced manipulation — •CARSTEN SPRODOWSKI, MICHAEL MEHLHORN, and KARINA MORGENSTERN — 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 tunnelling 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 electronical states of the molecules. For small energies (1500meV with 0.3 nA) the cluster reorders, 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 tunnelling 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.

O 93.4 Fri 11:00 MA 043

Modeling NO_x Storage Materials: Adsorption and interaction of NO_2 with BaO nanoparticles — •THORSTEN STAUDT[1], AINE DESIKUSUMASTUTI[1], SANDRA GARDONIO[2], SILVANO LIZZIT[2], ERIK VESSELLI[3], ALESSANDRO BARALDI[3], and JÖRG LIBUDA[1] — [1]Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen, Germany — [2]Sincrotrone Trieste, Italy — [3]Physics Department, University of Trieste, Italy

In order to obtain a fundamental understanding of the underlying processes of NO_x storage and reduction (NSR) catalysts we have studied the reaction of NO_2 with BaO nanoparticles supported on an ordered Al_2O_3 thin film on NiAl(110). We use a combination of high-resolution XPS obtained at the synchrotron radiation facility ELETTRA in Triest, vibrational spectroscopy (IRAS) and molecular beam (MB) techniques. Various nitrogen-oxo surface intermediates are identified by XPS and IRAS and the reaction behaviour shows a strong temperature dependence. At 300 K surface nitrites are formed and the conversion into surface nitrates occurs only at a very low rate. These reactions are only limited to the surface of the BaO particles. At 500 K the conversion into nitrates is more facile and nitrate formation proceeds beyond the particle surface, which yields to the formation of ionic nitrates.

Decomposition experiments exhibit that the stability of the barium nitrate nanoparticles is strongly depended on the particle size [1]. The larger particles are stable up to a temperature of 650 K, whereas the surface related species on small particles decompose at a temperature of 350-450 K. [1] A. Desikusumastuti et al., Catal. Lett., in press

O 93.5 Fri 11:15 MA 043

Internal exoemission in K/p-Si(001) Schottky diodes — •KORNELIA HUBA, DAVID KRIX, and HERMANN NIENHAUS — Fachbereich Physik, Universität Duisburg-Essen, Duisburg

Ultrathin potassium films of typically 1 nm thickness were deposited on hydrogen terminated p-Si(001) surfaces at low temperatures. Using a softly approached gold ball, an electric contact to the thin film was formed and current/voltage characteristics were recorded as a function of the substrate temperature. The K/p-Si contacts are Schottky diodes with low reverse currents of below 10 pA. Applying thermionic emission theory a homogeneous Schottky barrier height of 0.56 eV was determined. Oxidation of the K films by exposures to molecular oxygen leads to chemically induced electronic excitations. They were studied by measuring the internal exoemission currents, i.e. chemicurrents, in the diodes. The chemicurrent transients exhibit a maximum and less significant additional features after longer exposures. In addition to the current measurements, the oxygen uptake as well as the K film thickness and morphology were characterized by Auger electron spectroscopy and Kelvin probe measurements.

O 93.6 Fri 11:30 MA 043

Non-adiabatic Phenomena during Oxidation of K/Pd-Thin-Films on Silicon — •DAVID KRIX, KORNELIA HUBA, and HERMANN NIENHAUS — Fachbereich Physik, Universität Duisburg-Essen, Duisburg

Large area, nanometer thick Pd films were grown on silicon substrates. On H-terminated, Boron doped H:p-Si(001) surfaces a Schottky barrier height of $\Phi_p = 0.38\,eV$ could be extracted from I-V-measurements using thermionic emission theory. With nearly ideal behavior the diodes show reverse currents of below 1 nA at low temperatures of 120 K. Applying small amounts of K to the surface makes it highly sensitive to oxidizing gases. Similar to exoemission experiments, hot charge carriers are produced during oxygen exposure which can be measured as a chemicurrent, i.e. internal exoemission, flowing in a circuit involving the Schottky diode as a sensor.

Sensor parameters like K coverage and Pd film thickness were modified to study their influence on the time resolved chemicurrent transients. The total chemicurrent yield, i.e. the total amount of charge detected, was found to be exponentially attenuated with increasing Pd thickness at a constant value of $\lambda \approx 1.1\,nm$. Auger emission spec-

troscopy and Kelvin probe measurements were used to compare the evolution of the chemicurrents to the oxygen uptake of the samples.

O 93.7 Fri 11:45 MA 043

Particle size dependence of adsorption state and photodesorption of NO on AgNPs on thin alumina film —
•Daniel Mulugeta[1], Ki Hyun Kim[1], Kazuo Watanabe[1], Dietrich Menzel[1,2], and Hans-Joachim Freund[1] — [1]Fritz-Haber-Institute der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — [2]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 N_2O+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 (T_t=$\sim$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 T_t (up to $\sim$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.

O 93.8 Fri 12:00 MA 043

Chemicurrent studies on bimetallic surfaces — •Beate Schindler, Eckart Hasselbrink, and Detlef Diesing — Fachbereich Chemie and 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 ($5 \cdot 10^{15}$ 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 j_H. For strong chemisorption systems like Pt-H exponentially decaying chemicurrent traces ($e^{-j_H \cdot t}$) 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.

O 93.9 Fri 12:15 MA 043

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 NH_3 and D_2O, 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 D_2O 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 NH_3-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.

O 93.10 Fri 12:30 MA 043

Electronic valence band structure of V_2O_5 — •Torsten Stemmler, Maximilian Kauert, Helmut Dwelk, and Recardo Manzke — Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin

We will present high-resolution ARPES measurements of V_2O_5 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].
[1] A.Chakrabarti et al., Phys. Rev. B59, 10583 (1999)
[2] V.Eyert et al., Phys. Rev. B57, 12727 (1998)
[3] S.Shin, Phys. Rev. B41, 4993 (1990
[4] Q.Wu, Chem. Phys. Let. 430, 309 (2006)

O 93.11 Fri 12:45 MA 043

STM-induced Switching of Hydrogen on a Silicon(100) Surface: An Open-System Density Matrix Study — •Karl Zenichowski, Tillmann 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 Liouville-von 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].

[1] U.J. Quaade et al., Surf. Sci. **415**, L1037 (1998). [2] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976). [3] B.N.J. Persson, J.E. Demuth, Solid State Commun. **57**, 769 (1986). [4] B.N.J. Persson, A. Baratoff, Phys. Rev. Lett. **59**, 339 (1987). [5] K. Zenichowski, T. Klamroth, P. Saalfrank, in preparation.