

O 12: Surface dynamics

Time: Monday 16:00–19:15

Location: H 2013

O 12.1 Mon 16:00 H 2013

Density driven solidification of a 2D molecule gas on a bulk insulator: Co-Salen on NiO(001) — •JOSEF GRENZ, ALEXANDER SCHWARZ, and ROLAND WIESENDANGER — Institute of Applied Physics, University of Hamburg, Jungiusstr. 11, 20355 Hamburg

Co-Salen is a planar metal-organic Schiff base complex and known for its oxygen affinity and tendency to pair in dimers. Previous atomic force microscopy studies in UHV have shown, that this molecule initially adsorbs on NaCl(001) as monomers and with increasing coverage exhibits a bimodal island growth with dimers as building blocks [1,2]. However, on NiO(001), which also crystallizes in the rocksalt structure, for low coverages (< 1 ML) no growth can be detected, only step edge decoration. After complete decoration, diffusing molecules can be observed on flat terraces using $z(t)$ -spectroscopy on a fixed (x, y) -position: Whenever a molecule passes underneath the tip, its z -position is adjusted accordingly. Increasing the amount of deposited molecules leads to more frequent adjustment events. If the density of molecules becomes large enough, diffusion stops. High resolution AFM measurements at low temperatures reveal the formation of an amorphous monolayer consisting of monomers. After this density driven solidification of a molecule gas layer-by-layer step flow growth sets in.

- [1] S. Frey, *et al.*, Nanotechnology **20**, 405608 (2009).
- [2] K. Lämmle, *et al.*, Nano Lett. **10**, 2965 (2010).

O 12.2 Mon 16:15 H 2013

Signatures of non-adiabaticity in the scattering of O₂ at Ag(111)? — •ITZIAR GOIKOETXEA^{1,2}, JÖRG MEYER¹, J. INAKI JUARISTI², MAITE ALDUCIN², and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Centro de Física de Materiales, San Sebastián, Spain

We study the scattering of O₂ at Ag(111) using molecular dynamics techniques based on a six-dimensional first-principles adiabatic potential energy surface (PES). In preceding work [1] we had shown that the measured extremely low initial sticking coefficient at this surface can be rationalized by late and large energy barriers of 1.2 eV and an extremely narrow entrance channel leading to dissociation. Unfortunately, these adiabatic PES characteristics render the sticking a rather insensitive quantity with respect to an at times conjectured spin or charge non-adiabaticity in the O₂-Ag(111) interaction. We therefore now turn to the regime where the latter is brief and focus on the O₂ scattering properties. Intriguingly, the adiabatic simulations reproduce both in-plane and out-of-plane scattering data [2] even to the level of distinct features. These features have been interpreted as indications for two distinct scattering regions: a smooth surface region above the chemisorption well at large distances from the surface, and a more corrugated surface region at closer distances [2]. We qualify these interpretations and the underlying low-dimensional model conceptions based on our high-dimensional first-principles simulations.

- [1] I. Goikoetxea *et al.*, *accepted at New J. Phys.*
- [2] A. Raukema *et al.* J. Chem. Phys. **103**, 6217 (1995).

O 12.3 Mon 16:30 H 2013

Time-resolved laser-induced desorption of atomic Deuterium and Hydrogen from HOPG — •ROBERT FRIGGE and HELMUT ZACHARIAS — Physikalisches Institut, Universität Münster, Germany

Formation processes of molecular hydrogen upon radiation of adsorbed atoms on graphitic dust particles play an important role in the interstellar circuit of matter. However, the conversion process is still not fully understood yet.

Atomic hydrogen desorption from HOPG is examined after surface excitation with fs-laser pulses at $\lambda = 400$ nm. Desorbed neutral H atoms are ionized using (2+1) REMPI via the $2s \leftarrow 1s$ transition, and are detected with a time-of-flight mass spectrometer. Velocity distribution measurements result in three maxima for fast, medium and very slow desorbed hydrogen atoms. By electron scattering calculations [1] of the vibrational excitation of the H-C bond the three maxima can be addressed with different adsorption potentials, depending upon the neighboring H atom position on the graphene lattice [2,3]. A nonlinear fluence dependence of the desorption yield allows two pulse-correlation experiments. As a result we derive a pulse-delay dependent yield with a FWHM of about 700 fs with a coverage dependent variation. This correlation time indicates short lifetimes of the excited electrons and

supports a calculation in the DIMET model.

- [1] R. Frigge *et al.*, Phys. Rev. Lett., **104**, 256102 (2010)
- [2] L. Jelaica, V. Sidis, Chem. Phys. Lett., **300** 157 - 162 (1999)
- [3] L. Hornekær *et al.*, Phys. Rev. Lett., **97**, 186102 (2006)

O 12.4 Mon 16:45 H 2013

Non-adiabatic Effects in the Reaction of Chlorine Molecules with Potassium — •FELIX BECKER, DAVID KRIX, and HERMANN NIENHAUS — University of Duisburg-Essen and CeNIDE, Germany

The energy released in an exothermic chemical reaction of a gas molecule with a metal surface may be dissipated adiabatically by the creation of phonons or non-adiabatically by excitation of the electronic system. In the past, non-adiabatic effects in the reaction of Cl₂ with K were studied by exoelectron emission and chemiluminescence measurements only.

Here, we present XPS and chemicurrent data detecting low-energy holes as well as photons generated by the chlorination of potassium. Two kinds of large-area Schottky diodes were used as hot charge carrier detectors. The first were formed by direct deposition of K on H-terminated *p*-Si(111), the second had an intermediate silver layer between K and Si. For thin metal layers hot holes could be measured. They travel ballistically through the metal film and traverse the Schottky barrier if the kinetic energy is larger than the barrier height (typ. 0.4 eV). Chemiluminescence photons can be distinguished from hot holes by varying the metal film thickness as the mean free path (mfp) of the photons exceeds the mfp of hot holes. The metal film thickness dependent reverse currents strongly indicate that the presence of a rough silver film enhances the chemiluminescence during the reaction.

O 12.5 Mon 17:00 H 2013

Beating the heat atomistically: Watching phonons cool down during O₂ dissociation on Pd(100) — •JÖRG MEYER and KARSTEN REUTER — Technische Universität München, Germany

Energy conversion at interfaces is at the center of the rapidly growing field of basic energy science. One particular example is the conversion of chemical energy into heat which comes as an unavoidable by-product of all exothermic elementary reaction steps in heterogeneous catalysis. While engineers routinely deal with important consequences on a macroscopic scale based on well-known continuum theories and empirically determined effective parameters, an atomistic understanding is very limited at best. Aiming at multiscale modeling, our novel QM/Me approach extends the power of embedding techniques to metallic systems. A huge atomistically described bath can thus be included in *ab initio* molecular dynamics simulations of chemical reactions at catalyst surfaces. Applied to O₂ dissociation on Pd(100) as a representative showcase system, for which electron-hole pair excitations are unlikely to act as dominant primary energy dissipation channel [1], we quantify concomitant phonon excitations based on a newly developed projection scheme. Thanks to the phononic details implicitly incorporated in the bath, we obtain a high resolution for individual modes over the entire surface Brillouin zone. We can thus unravel the role of surface phonons as well as question the validity of the harmonic approximation for the solid during the dynamics – commonly employed in model Hamiltonians – from an unprecedented first-principles perspective.

- [1] J. Meyer and K. Reuter, New J. Phys. **13**, 085010 (2011)

O 12.6 Mon 17:15 H 2013

Dynamics of Vibrational Modes of Pb Adsorbate Layers on Si(111): Mode Conversion and De-Excitation — •ANNIKA KALUS, SIMONE WALL, SUNG SAKONG, TIM FRIGGE, ANJA HANISCH-BLICHARSKI, PETER KRATZER, MARTIN KAMMLER, and MICHAEL HORN-VON HOEGEN — Universität Duisburg-Essen

Ultrafast time resolved reflection high energy electron diffraction was used to study the vibrational dynamics of adsorbate layers upon excitation with a fs laser pulse in a pump probe setup. We employed the Debye-Waller effect $I = I_0 \exp(-\langle (\mathbf{u}\mathbf{k})^2 \rangle)$ to follow the temporal evolution of the vibrational amplitude $\mathbf{u}$ of the adsorbate atoms. The SIC($\sqrt{3} \times \sqrt{3}$) reconstruction of Pb on Si(111) was used as model system and excited by 50 fs, 800 nm laserpulses at a fluence of 4 mJ/cm². We observe two time constants of 100 ps and 3 ns for the vibrational de-excitation. With the $\mathbf{k}$ dependence of the Debye-Waller effect we

identified the fast decay as a mode with a dominant parallel amplitude while the slow mode exhibits a dominant vertical amplitude. Both time constants can be explained with classical molecular dynamics simulations. The electronic and phononic band structures of the substrate plus adsorbate layer were calculated using density functional theory. The hot electrons created by the laser pulse initially excite solely optical phonons. These parallel modes convert on a 100 ps time scale to modes perpendicular to the surface that dissipate their energy into the Si substrate on a ns time scale. This surprisingly long lifetime is explained by the small overlap between the low-energy vertical Pb modes with an energy of 2 - 4 meV and the Si acoustic phonons.

O 12.7 Mon 17:30 H 2013

Phonon density of states of ultra-thin europium films from in-situ 151Eu nuclear inelastic scattering — •OLGA BAUDER¹, MARTHE KAUFHOLZ², MARCHIN ZAJAC³, and SVETOSLAV STANKOV^{1,2} — ¹Laboratory for Applications of Synchrotron Radiation, KIT, Germany — ²Institute for Synchrotron Radiation, KIT, Germany — ³European Synchrotron Radiation Facility, Grenoble, France

It is well known that in thin films atoms vibrate in a manner significantly different as compared to the bulk. This is attributed to the broken translation symmetry and consequently to the reduced coordination of the surface atoms. For 3d metals these anomalies were investigated both theoretically and experimentally for the Fe(110) surface. However, there are no studies for the surfaces of 4f metals reported so far. We have investigated the phonon DOS of epitaxial ultra-thin Eu metallic films by in-situ nuclear inelastic scattering on 151Eu. The results reveal striking deviations of the phonon spectra of 1.1 nm thick film compared to that of bulk Eu. By reducing the film thickness, a systematic hardening, instead of softening of the phonon DOS is detected. * S.S. acknowledges the support by the Helmholtz Association for establishing a Helmholtz-University Young Investigator Group "Interplay between structure and dynamics in epitaxial rare earth nanostructures" (VH-NG-625).

O 12.8 Mon 17:45 H 2013

Watching It Freeze: Peierls Distortion of the In/Si(111) Surface — •SIMONE WALL¹, BORIS KRENZER¹, STEFAN WIPPERMANN², SIMONE SANNA², FRIEDRICH KLASING¹, ANJA HANISCH-BLICHARSKI¹, MARTIN KAMMLER¹, WOLF GERO SCHMIDT², and MICHAEL HORN-VON HOEGEN¹ — ¹University of Duisburg-Essen and CeNIDE, Duisburg, Germany — ²Paderborn University, Paderborn, Germany

TR-RHEED was employed to investigate the dynamics of the Peierls-instability-driven phase transition on the (8x2) In/Si(111) surface. Far below the critical temperature of 90K, the (8x2)-(4x1) phase transition is electronically driven through weak excitation with a fs-laser pulse and results in a long-lasting super-cooled excited (4x1) phase. This metastable situation far away from equilibrium is only accessible through the excitation by the fs-laser pulse. A thermal excitation of the phase transition due to laser induced heating was experimentally excluded. The recovery of the (8x2) ground state on a timescale of 500 ps is triggered by adsorbates that act as nucleation seeds - the same way that super-cooled water in a bottle freezes upon the insertion of seeds. With increasing density of adsorbates the recovery to the groundstate proceeds much faster. Density functional theory calculations reveal the microscopic scenario of the phase transition, which occurs one-dimensionally along the Indium chains. The surface unit cells fall back into their ground state one at a time, like a row of falling dominoes. The phase front propagates at about 800 m/s, comparable to the speed of sound.

O 12.9 Mon 18:00 H 2013

Probing diffusion of single nanoparticles at water/oil interfaces with fluorescence correlation spectroscopy — DAPENG WANG, HANS-JÜRGEN BUTT, and •KALOIAN KOYNOV — Max Planck Institute for Polymer Research, Mainz, Germany

A good understanding of the dynamics and self organization of nanometer-sized objects, e.g., molecules, macromolecules and nanoparticles (NPs) at immiscible liquid/liquid interfaces is not only of fundamental interest for the soft matter physics and cell biology, but is also very important for a number of technological applications in material synthesis, pharmacy, microfluidics and nanotechnology. Here, we show that the fluorescence correlation spectroscopy (FCS), a method based on measuring the fluctuations of the fluorescent light intensity caused by the diffusion of fluorescent species through a very small observation volume, is very well suited for studies of NPs diffusion on liquid/liquid interfaces as it offers the possibility to monitor fast diffusing, nanome-

ter size objects at extremely low surface coverage. We used FCS to study the diffusion of fluorescent semiconductor nanoparticles (quantum dots) on planar water/oil interfaces. The effects of several important parameters, i.e. the particles size, their surface functionalization (hydrophobic/hydrophilic) and the oil phase viscosity were systematically explored. Most notably, a significant slow-down of nanoparticle diffusion at the water/oil interface was observed. The effect was most evident when the viscosities of both liquid phases were similar, i.e. at the water/decane interface.

O 12.10 Mon 18:15 H 2013

Heat Transport from Self Organised Ge Nano-Structures to Si(001) Substrate — •TIM FRIGGE, ANJA HANISCH-BLICHARSKI, SIMONE WALL, ANNIKA KALUS, MARTIN KAMMLER, and MICHAEL HORN-VON HOEGEN — University of Duisburg-Essen and CeNIDE, Duisburg, Germany

We used ultrafast time-resolved reflection high energy electron diffraction to investigate the heat transport from nanoscale Ge clusters to a Si(001) substrate. From the transient cooling behaviour upon fs-laser excitation the thermal properties of these nanostructures could be determined without further calibration. On Si(001) Ge grows in a Stranski-Krastanov mode and can be used for self organisation of nanostructures. Island formation occurs at a critical coverage of 3 monolayers with metastable hut-clusters of a width of 25nm and a height of 2.5nm. Further Ge deposition results in the formation of 50 nm wide dome-clusters with a height of 6nm. Both cluster-types exhibit atomically flat side facets, are mono-crystalline, epitaxial, defect-free, and have a uniform size distribution. The interface between the Ge-islands and the Si(001)-substrate is abrupt. At a base temperature of 25K and a transient heating by 100K, caused by the fs laser pump-pulse, different cooling rates for both clusters were determined. Hut-clusters cool in 50ps while dome-clusters cool three times slower in 150ps. A comparison with the theoretically expected thermal boundary conductance of the diffuse mismatch model (DMM) for two-dimensional uniform Ge layers shows that the cooling rate of the nano scale islands is reduced by more than a factor two!

O 12.11 Mon 18:30 H 2013

Ultrafast Electron Dynamics in the Topological Insulator Material Bi₂Se₃ — •PATRICK KIRCHMANN^{1,2}, JONATHAN SOBOTA^{2,3,4}, SHUOLONG YANG^{2,3,4}, JAMES ANALYTIS^{2,3}, YULIN CHEN^{2,3,4}, IAN FISHER^{2,3}, and ZHI-XUN SHEN^{2,3,4} — ¹Fritz Haber Institute of the Max Planck Society, Department of Physical Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany — ²Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA — ³Geballe Laboratory for Advanced Materials, Department of Applied Physics, Stanford University, Stanford, CA 94305, USA — ⁴Department of Physics, Stanford University, Stanford, CA 94305, USA

Using femtosecond time- and angle-resolved photoemission spectroscopy, we investigated the non-equilibrium electron dynamics of the topological insulator Bi₂Se₃. We studied p-type Bi₂Se₃, in which the metallic Dirac surface state and bulk conduction bands are unoccupied. Optical excitation leads to a meta-stable population at the bulk conduction band edge, which feeds a population of the surface state persisting for > 10 ps. This unusually long-lived population of a metallic Dirac surface state with spin texture may present a channel in which to drive transient spin-polarized currents.

O 12.12 Mon 18:45 H 2013

Two-photon photoemission studies Germanium(100) - Binding energies, lifetimes and dispersion of the surface states — •JENS KOPPRASCH^{1,2}, KRISTOF ZIELKE^{1,2}, CORNELIUS GAHL^{1,2}, CHRISTIAN EICKHOFF^{1,2}, JÖRG SCHÄFER³, and MARTIN WEINELT^{1,2} — ¹Max-Born-Institut, Max-Born-Straße 2a, 12489 Berlin, Germany — ²Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany — ³Universität Würzburg, Fakultät für Physik und Astronomie, Am Hubland, 97074 Würzburg, Germany

Germanium(Ge) has the same crystal structure as silicon (diamond-like) but opposite to Si the band gap is much smaller (0.67 eV at 300 K) and has a local minimum at the Γ -point. This difference in band structure leads to a growing interest of Ge in semiconductor industry, where it is used for solar cells, high-power transistors, infrared optics and x-ray detectors.

The surface reconstruction on Ge(100) is also comparable to Si(100). This leads to the so-called dangling-bond states D_{up} and D_{down} . By using two-photon-photoemission (2PPE) spectroscopy we observed

both surface states and could identify the first image-potential state $n=1$. Binding energies, lifetimes and dispersion of these states will be presented. Measurements at 90K within a range of $k_{\parallel} = \pm 0.5 \text{ \AA}^{-1}$ and a maximum time delay of 50ps show the conduction band minimum and a number of transitions among the bulk bands. We will present this measurements and discuss their origin and the concomitant carrier dynamics.

O 12.13 Mon 19:00 H 2013

Excitonic features in image-potential resonances on Si(100) probed by two-photon photoemission — •MARTIN WEINELT^{1,2}, CHRISTIAN EICKHOFF^{1,2}, and CORNELIUS GAHL^{1,2} — ¹Max-Born-Institut, Max-Born-Straße 2a, 12489 Berlin, Germany — ²Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany

Electronic transitions into unoccupied image-potential resonances $n = 1$ and $n = 2$ on silicon(100) were studied with angle-resolved femtosecond pump-probe photoelectron spectroscopy. Off-resonant excitation out of valence bands unveils the typical behavior of electrons trapped in the image-potential in front of a surface, characterized by a well-defined binding energy [1] and an effective mass of 1. However, tuning the excitation energy of the pump-pulse across the resonance between the occupied dangling-bond D_{up} and unoccupied $n = 1, 2$ surface states reveals excitonic features, both in the dispersion and the binding energy of the probed state. As photoemission probes the population of specific states, resonant excitation out of the discrete D_{up} surface state implies the formation of a surface exciton population on a femtosecond timescale.

[1] P. M. Echenique and J. B. Pendry, J. Phys. C **11**, 2065 (1978)