

O 96: Ultrafast Electron Dynamics at Surfaces and Interfaces

Time: Friday 10:30–12:45

Location: MA 004

Invited Talk

O 96.1 Fri 10:30 MA 004

Ultrafast electron dynamics at oxide surfaces: How metallic is a semiconductor? — ●JULIA STÄHLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dept. of Physical Chemistry, Faradayweg 4-6, 14195 Berlin, Germany

Light absorption in a semiconductor creates non-equilibrium conditions that relax by a multitude of pathways involving electron dynamics on femto- and picosecond timescales. These can be monitored in real time using time-resolved one- and two-photon photoelectron spectroscopy of the occupied and unoccupied electronic structure, respectively. On ZnO(10 $\bar{1}$ 0), hydrogen adsorption causes the formation of a charge accumulation layer through downward surface band bending. Despite this metallicity, highly stable sub surface-bound excitons form within only 200 fs after above band gap photoexcitation. Strong excitation close to the Mott limit enhances the screening of the Coulomb interaction (CIA) and reduces the exciton formation probability [1]. On the other hand, in the case of the strongly correlated electron material VO₂, strong photoexcitation even leads to an *instantaneous collapse* of the band gap, followed by hot carrier relaxation within 200 fs. In conjunction with many body perturbation theory, these results show that the photoinduced semiconductor-to-metal transition is caused by photohole doping at the top of the VO₂ valence band: The significantly enhanced screening of the CIA through low-energy intraband transitions causes the drastic band gap renormalization [2].

[1] J.-C. Deinert et al., *Phys Rev Lett* **113**, 057602 (2014)

[2] D. Wegkamp, M. Herzog et al., *Phys Rev Lett* **113**, 216401(2014)

O 96.2 Fri 11:00 MA 004

Electron dynamics across the charge-transfer gap of NiO ultrathin films — ●KONRAD GILLMEISTER¹, MARIO KIEL¹, and WOLF WIDDRA^{1,2} — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

NiO is known as a prototype system for a strongly correlated oxide. Despite of numerous scientific investigations of its electronic structure, studies of the electron dynamics of NiO are rare. This contribution deals with the unoccupied Ni 3d states at the upper edge of the charge-transfer gap. For the study, ultrathin well-ordered films from 1–20 monolayers (ML) thickness have been grown on Ag(001) via molecular beam epitaxy.

The unoccupied Ni 3d states have been investigated by time-resolved two-photon photoemission spectroscopy. While interface effects dominate the electronic structure for films up to 3 ML, films of 4 ML and beyond show bulk-like behavior. For these thicknesses we find the upper Hubbard band (UHB) at 2.5 eV above E_F . Electrons excited into the UHB decay on a timescale of less than 15 fs. The surprisingly short lifetimes are explained by correlation effects within the oxide film. Ultrafast decay via additional intra-gap states and strong electron-phonon coupling is also considerable.

O 96.3 Fri 11:15 MA 004

Charge Transfer Dynamics at the Buried GaP/Si(001)-Interface Studied by Means of Time-Resolved SHG — ●ALEXANDER LERCH, KRISTINA BRIXIUS, ANDREAS BEYER, KERSTIN VOLZ, WOLFGANG STOLZ, and ULRICH HÖFER — Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg

Epitaxially grown GaP on Si(001) is a technologically important and structurally well characterized model system for a polar/nonpolar semiconductor interface. We have employed time-resolved optical second-harmonic generation (SHG) to investigate the ultrafast carrier dynamics at the buried GaP/Si interface. The experiments were conducted using 800-nm 45-fs pump and probe pulses in a non-collinear geometry where the SHG response of bulk GaP is suppressed. The samples exhibit characteristic SHG transients on a 5-ps time-scale which are attributed to the build-up of an electric field via charge transfer across the interface. From the linear dependence of the transients on the pump fluence we exclude direct excitation of both GaP and Si bulk with direct band gaps of 2.8 eV and 3.4 eV, respectively. Instead we propose a direct excitation of electronic states at the interface by the 1.55-eV pump pulses which is consistent with a rise-time of the SHG signal faster than 30 fs. We also show, how different SHG

components of the interface can be distinguished phase-sensitively by utilizing interference between SHG from GaP bulk and the transients, and discuss the influence of the lattice temperature on the dynamics via electron-phonon scattering.

O 96.4 Fri 11:30 MA 004

One-step theory of pump-probe photoemission — ●JÜRGEN BRAUN¹, ROMAN RAUSCH², MICHAEL POTTHOFF², JAN MINÄR¹, and HUBERT EBERT¹ — ¹Dept. Chemie, LMU Universität München, Germany — ²I. Institut für Theoretische Physik, Universität Hamburg, Germany

A theoretical frame for the description of pump-probe photoemission is presented. The approach is based on a general formulation using the Keldysh formalism for the lesser Green function to describe the real-time evolution of the electronic degrees of freedom in the initial state after a strong pump pulse that drives the system out of equilibrium. The final state is represented by a time-reversed low-energy electron diffraction (LEED) state. Our one-step description is related to Pendry's original formulation of the photoemission process as close as possible. The formalism allows for a quantitative calculation of the time-dependent photocurrent in particular for simple metals where a picture of effectively independent electrons is assumed as reliable. The theory is worked out for valence- and core-electron excitations [1]. As a first application, the theoretical description of two-photon photoemission for real systems within the KKR-approach is introduced [2].

1. J. Braun, R. Rausch, M. Potthoff, J. Minär, H. Ebert, submitted to *Phys. Rev. B* (2014)

2. H. Ebert et al., The Munich SPR-KKR package, version 6.3, <http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR> (2012)

O 96.5 Fri 11:45 MA 004

Attosecond delays in the photoemission from layered materials — SERGEJ NEB¹, FABIAN SIEK¹, MATTHIAS HENSEN¹, SEBASTIAN FIECHTER², HUGO DIL³, NORBERT MÜLLER¹, ●WALTER PFEIFFER¹, and ULRICH HEINZMANN¹ — ¹Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany — ²Helmholtz Zentrum Berlin, Institut für Solare Brennstoffe, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ³Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

The availability of single attosecond (as) XUV pulses allows investigating ultrafast electron dynamics on the as time scale by recording slight temporal shifts of the photoelectron streaking in a simultaneously present strong IR field. The physical origin of the observed small delays is not yet understood and controversial theoretical models coexist demonstrating our still limited understanding of the fundamentals of the photoemission process. We report delays for core level emissions from different layered materials with and without inversion symmetry. This provides a larger data base for testing the various theoretical models. In particular solids with defined layers of different chemical composition allow an investigation of the influence of propagation effects and of photoelectron wave phase shifts.

O 96.6 Fri 12:00 MA 004

Ultrafast charge transfer across the 5P-pyridine/ZnO(10 $\bar{1}$ 0) interface — ●JAN-CHRISTOPH DEINERT¹, CLEMENS RICHTER¹, LEA BOGNER¹, YVES GARMSHAUSEN², STEFAN HECHT², MARTIN WOLF¹, and JULIA STÄHLER¹ — ¹Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — ²Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

The functionality of hybrid inorganic organic systems (HIOS) is governed by the interfacial electronic coupling and the resulting charge transfer (CT) dynamics. To gain direct insight into these dynamics we use femtosecond time-resolved two-photon photoemission (2PPE) to investigate the hybrid system 5P-pyridine on ZnO(10 $\bar{1}$ 0). The molecules form an ordered layer on the mixed-terminated ZnO surface, accompanied by a strong reduction of the work function by up to 1.8 eV. We optically excite electrons from just below the Fermi level E_F at the ZnO surface with 2.5 eV photons, leading to transient formation of a CT state by population of the molecular LUMO (1.7 eV above E_F). This CT state is used to observe the *pure* interfacial electron transfer from the LUMO to the ZnO conduction band, which oc-

curs on an ultrafast timescale of 90 fs. This is in contrast to previous results on interfacial CT processes on ps timescales at ZnO interfaces where photoexcitation is used to create *excitons* in the organic film. [1] Our results show that the purely electronic coupling at the interface is significantly stronger in the absence of the photohole.

[1] K. R. Siefermann *et al.*, *J. Phys. Chem. Lett.* **5**, 2753–2759 (2014)

O 96.7 Fri 12:15 MA 004

Theoretical Study of Ultrafast Electron Transfer in Alkanethiolate Self-Assembled Monolayers at the Au(111) Surface

— •VERONIKA PRUCKER¹, PEDRO B. COTO¹, MICHEL BOCKSTEDTE¹, HAOBIN WANG², and MICHAEL THOSS¹ — ¹Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 7/B2, D-91058 Erlangen, Germany — ²Department of Chemistry, University of Colorado, Denver, CO 80217, USA

The dynamics of ultrafast electron transfer (ET) processes in self-assembled monolayers consisting of nitrile substituted short-chain alkanethiolate molecules on gold substrates is investigated. Employing a model Hamiltonian, which is parametrized by first principles electronic structure calculations [1], and dynamical simulations, we analyze the basic mechanism underlying the ET process. The results show, in accordance with experiments [2,3], a dependence on the molecular chain length and on the symmetry of the donor states [4]. Additionally, we discuss the influence of partly occupied substrate states at the Fermi edge on the ET process.

[1] I. Kondov *et al.*, *J. Phys. Chem. C* **111**, 11970 (2007).

[2] F. Blobner *et al.*, *J. Phys. Chem. Lett.* **3**, 436 (2012).

[3] P. Kao *et al.*, *J. Phys. Chem. C* **114**, 13766 (2010).

[4] V. Prucker *et al.*, *J. Phys. Chem. C* **117**, 25334 (2013).

O 96.8 Fri 12:30 MA 004

Dynamics of exciton formation and decay in SP6 films on ZnO(10-10)

— •LEA BOGNER, LAURA FOGLIA, JAN-CHRISTOPH DEINERT, CLEMENS RICHTER, MARTIN WOLF, and JULIA STÄHLER — Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Zinc oxide (ZnO) is a promising transparent electrode material for various optoelectronic applications. On the ZnO surface, the spirofluorene derivative SP6 forms smooth amorphous films from which, after resonant excitation, charge transfer to the ZnO conduction band has been observed [1]. We investigate the electronic properties and the excited states dynamics of 20 nm thick SP6 films adsorbed on ZnO(10-10) using time-resolved two-photon photoemission (2PPE). In this system, optical spectroscopy showed that resonant excitation of the SP6 molecules leads to the formation of an excitonic state which relaxes vibrationally (2-6 ps) and decays on a timescale of 200-300 ps [2]. Complementarily, time-resolved 2PPE provides access to absolute binding energies and fast electron dynamics on fs timescales, which we attribute to exciton formation. Photon energy and repetition rate-dependent measurements indicate a strong intermolecular coupling of the excited states leading to electron emission from a long-lived dark state (1 eV above E_F) due to energy transfer rather than photoemission by the probe pulse. Possible energy transfer mechanisms such as intermolecular Coulombic decay or Förster resonance energy transfer will be discussed.

[1] S. Blumstengel *et al.*, *Phys. Rev. B* **77**, 085323, 2008

[2] L. Foglia *et al.*, to be published