

## O 97: Ultrafast Electron Dynamics at Surfaces and Interfaces III

Time: Friday 10:30–13:00

Location: H16

O 97.1 Fri 10:30 H16

**The transient modification of a ZnO surface upon photoexcitation** — ●LUKAS GIERSTER, SESHA VEMPATI, and JULIA STÄHLER — Fritz-Haber-Institut Berlin, Dpt. Phys. Chem.

ZnO is intensely explored due to its great potential especially in the field of optoelectronics and (photo-) chemistry. However, it is still under debate how the properties of ZnO vary with photoexcitation [1]. Here, we use time- and angle resolved photoelectron spectroscopy to investigate the transient electronic properties of the ZnO (10-10) surface under resonant photoexcitation of the band gap. At low excitation densities, a small additional signal below the Fermi level is observed, consistent with the previously observed surface exciton formation [2]. Above the Mott density, within about 60 fs an intense spectral feature builds up which exhibits the characteristics of a thermalized electron gas. Likely, this new state results from bending the conduction band below the Fermi level by band gap renormalization: The ZnO surface becomes transiently metallic for hundreds of picoseconds. For all excitation densities a fraction of the pump-induced electronic population survives the inverse repetition rate of the laser (5  $\mu$ s). The photostationary population must be stabilized by a positive localized charge. Potential candidates are defects and photogenerated hole polarons, as recently observed for ZnO (10-10) [1]. [1] H. Sezen et al, Nat. Comm. 6, 6901 (2015) [2] J.-C. Deinert et al., PRL 113, 057602 (2014)

O 97.2 Fri 10:45 H16

**Time Resolved Photoemission Study of the Charge Transfer Dynamics in Anatase TiO<sub>2</sub>(101) for CO Photooxidation to CO<sub>2</sub>** — ●MICHAEL WAGSTAFFE<sup>1</sup>, HESHMAT NOEI<sup>1</sup>, SIMON CHUNG<sup>1</sup>, LUKAS WENTHAUS<sup>2,3</sup>, GUILHERME SEMIONE<sup>1</sup>, STEFFEN PALUTKE<sup>2,3</sup>, GIUSEPPE MERCURIO<sup>2,3</sup>, SIARHEI DZIARZHYTSKI<sup>1</sup>, HARALD REDLIN<sup>1</sup>, NICOLAI KLEMKE<sup>2</sup>, YUDONG YANG<sup>2</sup>, ANNE-LAURE CALENDRON<sup>2</sup>, FRANZ KÄRTNER<sup>2</sup>, WILFRIED WURTH<sup>1,2,3</sup>, and ANDREAS STIERLE<sup>1,3</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron, Notkestr. 85, 22607 Hamburg, Germany — <sup>2</sup>Center for Free-Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany — <sup>3</sup>Department Physik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Until recently, severe limitations have been placed on understanding the behavior of the photogenerated charge carriers in the photooxidation of CO to CO<sub>2</sub> on TiO<sub>2</sub> surfaces due to the ultrafast nature of the reaction. With their unprecedented temporal resolution, FELs allowed new insight to be obtained that has hitherto been unattainable. By applying ultra-fast optical pump-soft X-ray probe experiments at FLASH in DESY, we have obtained first insight into the activation mechanism of CO photooxidation on anatase TiO<sub>2</sub>(101). By using an optical laser of 800 nm and a FEL energy of 647.8 eV, the changes in the Ti 2p, O 1s and C 1s core levels have been monitored on a picosecond timescale. For the first time, the photooxidation of CO to CO<sub>2</sub> has been observed at two distinct time points of 2.1 ps and 7.3 ps, which we attribute to the charge carriers interacting with different adsorption modes of O<sub>2</sub> on the surface.

O 97.3 Fri 11:00 H16

**Probing long-range structural dynamics of surfaces by umklapp process assisted time-resolved low-energy photoelectron spectroscopy** — ●STEPHAN JAUERNIK, PETRA HEIN, MAX GURGEL, JULIAN FALKE, and MICHAEL BAUER — Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Germany

Laser-based angle-resolved photoelectron spectroscopy is performed on tin-phthalocyanine (SnPc) adsorbed on silver Ag(111). Upon adsorption of SnPc, strongly dispersing bands are observed which are identified as secondary Mahan cones formed by surface umklapp processes acting on photoelectrons from the silver substrate as they transit through the ordered adsorbate layer. We show that the photoemission data carry quantitative structural information on the adsorbate layer similar to what can be obtained from a conventional low-energy electron diffraction (LEED) study. More specifically, we compare photoemission data and LEED data probing an incommensurate-to-commensurate structural phase transition of the adsorbate layer. Based on our results we propose that Mahan-cone spectroscopy operated in a pump-probe configuration can be used in the future to probe structural dynamics at surfaces with a temporal resolution in

the sub-100-fs regime.

- [1] S. Jauernik, P. Hein et al., Phys. Rev. B 97, 125413 (2018)  
[2] G.D. Mahan, Phys. Rev. B 2, 4334 (1970)

O 97.4 Fri 11:15 H16

**Exciton dynamics and energy transfer at PTCDA/noble-metal interfaces** — ●KLAUS STALLBERG and ULRICH HÖFER — Fachbereich Physik, Philipps-Universität, D-35032 Marburg

Combining time-resolved photoluminescence (TRPL) and two-photon photoemission (2PPE) we investigate thin layered films of PTCDA on the (111) surfaces of silver and gold. Our combined experimental approach enables us to study the exciton dynamics from optical excitation in the organic layers to annihilation at the organic/metal interface. More specifically, we identify three different excitonic states – a monomer-related Frenkel exciton, a charge-transfer (CT) exciton, and an excimer – based on their spectral signatures and their radiative lifetimes in TRPL. 2PPE spectra of the same samples exhibit distinct low-energy features which we attribute to hot conduction electrons at the metal surfaces. The exciton dynamics, as probed with TRPL, strongly depends on the PTCDA film thickness which is varied from several nanometers down to a single monolayer. The decrease of the CT exciton radiative lifetime with decreasing film thickness is explained in terms of exciton diffusion along the stacking direction of the PTCDA molecules. Interestingly, exactly the same dependence on the PTCDA film thickness is observed for the hot-electron dynamics, as probed with 2PPE. This strongly points to the CT excitons as source of hot electrons after diffusion to the organic/metal interface. This energy transfer is found much more efficient on Ag(111) than on Au(111) indicating involvement of the metal-organic interface state of PTCDA/Ag(111) which is absent at the PTCDA/Au(111) interface.

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**Ultrafast charge carrier dynamics at the interface F4TCNQ:H-Si(111) from real-time TDDFT** — ●MATHEUS JACOBS, JANNIS KRUMLAND, ANA M. VALENCIA, and CATERINA COCCHI — Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

The electronic structure of inorganic surfaces can be effectively modified by the adsorption of molecular acceptors acting as dopants. As a result, their interaction with light can give rise to charge-transfer excitations at the interface, making the systems potentially appealing for optoelectronic applications. To this end, gaining insight and control on the dynamics of the photo-excited charge-carrier population is an essential task. Here, we consider the interface formed by the strong electron acceptor F4TCNQ adsorbed on the hydrogenated Si(111) surface, which was recently characterized both theoretically and experimentally [1]. The linear absorption spectrum of this system exhibits two maxima in the visible region corresponding to transitions between electronic states hybridized across the interface. In the framework of real-time time dependent density functional theory, as implemented in the octopus code [2], we investigate the charge-carriers dynamics induced by a laser pulse in resonance with each excitation and analyze the time evolution of the photoexcited electronic population. Our results offer insight into the earliest stage formation of optical excitations at hybrid interfaces.

- [1] H. Wang, et al. arXiv:1811.00037 (2018).

- [2] A. Castro, et al. Phys. Stat. Sol. B 243, 2465 (2006)

O 97.6 Fri 11:45 H16

**Relaxation of electronically confined states from Master Equation with first-principles-derived rates** — ●PETER KRATZER, MAEDEH ZAHEDIFAR, and SEBASTIAN SCHREIBER — Fakultät für Physik, Universität Duisburg-Essen

Atomically thin films of Pb on Si(111) provide an experimentally tunable system comprising both dispersive bands with metallic character and confined, thickness-dependent quantum well states. The lifetime of excited electrons in Pb films is limited by both electron-electron (e-e) and electron-phonon (e-ph) scattering. We employ the description by a Master equation for the electronic occupation numbers to analyse the relative importance of both scattering mechanisms. The electronic and phononic band structures, as well as the matrix elements for electron-phonon coupling within deformation potential theory were obtained

from density functional calculations. The contribution of impact ionization processes to the lifetime is estimated from the imaginary part of the electronic self-energy calculated in the GW approximation. By numerically solving the rate equations for the occupations of the Pb-derived electronic states coupled to phononic heat baths, we can follow the distribution of the electronic excitation energy to the various modes of Pb lattice vibrations. While e-e scattering is the dominant relaxation mechanism, we demonstrate that the e-ph scattering is highly mode-selective, with a large contribution from surface phonons. The time scales extracted from the simulations are compared to experimental data from time-resolved pump-probe experiments.

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O 97.7 Fri 12:00 H16

**Resonant charge transfer and energy dissipation during scattering of  $H^+$ /Al(111) studied with TDDFT and adiabatic GGA** — ●LUKAS DEUCHLER, CHRISTOPHER MAKAIT, and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany

Ab initio molecular dynamic simulations employing time-dependent density functional theory to describe the electron dynamics combined with Ehrenfest dynamics for the nuclei [1] within the limitation due to the approximate XC potential facilitate the investigation of resonant charge transfer during ion neutralization and electron-hole pair excitation at surfaces [2]. We have studied the scattering of hyperthermal  $H^+$  and  $H$ /Al(111) (for which experimental [3] and theoretical [4,5] results are available for comparison). Simulations have been performed with the code octopus [1] by A. Rubio et al. Charge and energy transfer and the excitation spectra have been compared for  $H^+$  and  $H$  impinging on the Al substrate. Tight-binding simulations [6] with input derived from TDDFT are capable of reproducing the charge transfer dynamics. In-detail analysis of the simulation results allows to pinpoint remaining open questions.

- [1] Andrade et al., Phys Chem Chem Phys **17**, 31371 (2015),
- [2] Zhao et al., Phys Condens Matter **27**, 025401 (2015),
- [3] Winter, Phys Condens Matter **8**, 10149 (1996),
- [4] Merino et al., Phys Rev B **54**, 15 (1996),
- [5] Lindenblatt et al., Nucl Instrum Meth Phys B **246**, 333 (2006),
- [6] Brako and Newns, Vacuum **32**, 1 (1982).

O 97.8 Fri 12:15 H16

**Microscopic energy flow dynamics in Fe/MgO** — ●NICO ROTHENBACH<sup>1</sup>, MARKUS E. GRUNER<sup>1</sup>, KATHARINA OLLEFS<sup>1</sup>, PING ZHOU<sup>1</sup>, CAROLIN SCHMITZ-ANTONIAK<sup>2</sup>, NIKO PONTIUS<sup>3</sup>, ROLF MITZNER<sup>3</sup>, CHRISTIAN SCHÜSSLER-LANGEHEINE<sup>3</sup>, ROSSITZA PENTCHEVA<sup>1</sup>, KLAUS SOKOLOWSKI-TINTEN<sup>1</sup>, RENKAI LI<sup>4</sup>, MIANZHEN MO<sup>4</sup>, SUJI PARK<sup>4</sup>, XIAOZHEN SHEN<sup>4</sup>, STEPHEN WEATHERSBY<sup>4</sup>, JIE YANG<sup>4</sup>, XIJIE WANG<sup>4</sup>, HEIKO WENDE<sup>1</sup>, UWE BOVENSIEPEN<sup>1</sup>, and ANDREA ESCHENLOHR<sup>1</sup> — <sup>1</sup>University Duisburg-Essen and CENIDE — <sup>2</sup>FZ Jülich — <sup>3</sup>Helmholtz-Zentrum Berlin — <sup>4</sup>SLAC

A localized optical excitation of a metal/insulator heterostructure, like a Fe/MgO multilayer, by a femtosecond (fs) laser pulse induces ultrafast dynamics like charge and spin transfer processes as well as coupling to low energy excitations mediated by e.g. electron-electron and electron-phonon scattering. We measure fs time- and element-resolved soft x-ray spectroscopy to separate and identify the electronic and lattice excitations. The latter is also analyzed by complementary ultrafast electron diffraction experiments. The response at the Fe  $L_3$ -edge is

maximal at 200 fs and represents local electronic excitations, coupling to phonons in Fe, and their relaxation to the insulator. The dynamics at the O K-edge reaches a maximal change after 400 fs, explained by lattice excitations of MgO due to energy transfer from Fe. Probing the O pre-edge gives rise to the interface states dynamics and deepens our understanding further. DFT calculations of layer-resolved vibrational and electronic DOS consolidate our interpretation. We acknowledge financial support by the DFG through the SFB1242.

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**Dynamics of optical excitations in a Fe/MgO(001) heterostructure from time-dependent density functional theory** — ●MARKUS ERNST GRUNER, ELAHEH SHOMALI, and ROSSITZA PENTCHEVA — Faculty of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, Germany

In the framework of real-time time-dependent density functional theory (RT-TDDFT) we unravel the layer-resolved dynamics of the electronic structure of a  $(Fe)_1/(MgO)_3(001)$  multilayer system after an optical excitation with a frequency below the band gap of bulk MgO. Substantial transient changes to the electronic structure, which persist after the duration of the pulse, are observed in particular for in-plane polarized electric fields, corresponding to a laser pulse arriving perpendicular to the interface. While the strongest charge redistribution takes place in the Fe layer, a time-dependent change in the occupation numbers is visible in all layers, mediated by the presence of interface states. The time evolution of the layer-resolved occupation numbers indicates a strong orbital dependence with the depletion from in-plane orbitals (e.g.  $d_{x^2-y^2}$  of Fe) and accumulation in out-of-plane orbitals ( $d_{z^2}$  of Fe and  $p_z$  of apical oxygen). We also see a small net charge transfer away from oxygen towards the Mg sites even for MgO layers, which are not directly in contact with the metallic Fe.

Financial support from the DFG within SFB 1242 (project C02) is gratefully acknowledged.

O 97.10 Fri 12:45 H16

**Local and Non-Local Relaxation Dynamics of Hot Electrons in Au/Fe/MgO(001)** — ●YASIN BEYAZIT<sup>1</sup>, JAN BECKORD<sup>1</sup>, JOHN THOMAS<sup>1</sup>, PING ZHOU<sup>1</sup>, DETLEF DIESING<sup>2</sup>, MANUEL LIGGES<sup>1</sup>, and UWE BOVENSIEPEN<sup>1</sup> — <sup>1</sup>Faculty of Physics, University of Duisburg-Essen, 47048 Duisburg, Germany — <sup>2</sup>Faculty of Chemistry, University of Duisburg-Essen, 45141 Essen, Germany

Photo-excited, hot electrons in multilayer thin films exhibit local and non-local dynamics which lead to relaxation and transport effects. The investigation of their interplay is so far mainly based on all-optical measurements. We present a novel tool for energy-resolved analysis of local and non-local relaxation dynamics in condensed matter. By using a back-pump/front-probe experimental configuration in femtosecond time-resolved, two-photon photoemission (tr-2PPE), we aim at separating these relaxation processes. The tr-2PPE intensity provides the relaxation time  $\tau$  and the delay of the maximum intensity  $t^*$ , and, thus, independent observables which we discuss in terms of inelastic relaxation and ballistic transport. We show first results for Au/Fe/MgO(001) and (i)  $\tau$  as a function of energy  $E - E_F$  as well as Au thickness  $d_{Au}$  and (ii)  $t^*$  regarding energy-resolved transport velocities of hot electrons. The proportionality between  $t^*$  and Au thickness points strongly towards ballistic transport. Our obtained velocities are in a good agreement with the literature values. This study was funded by the DFG through SFB1242.