1. Overview

The main focus of the present project is the geometric and electronic structure of solid and liquid surfaces and their response to excitation by femtosecond laser pulses. The research topics range from single electron dynamics at ferromagnetic metal and semiconductor surfaces to the collective response of the electronic system to intense laser excitation close to or above the ablation threshold. Thereby the coupling of electronic excitations to nuclear motion is studied following e.g. electron solvation in aqueous solutions, phase transitions in solids and at their surfaces and eventually material removal.

2. Subprojects and collaborations

UP1: Dynamics at surfaces studied by laser-synchrotron pump-probe experiments, in collaboration with W. Widdra (Univ. Halle)

UP2: Electron dynamics at semiconductor surfaces, in collaboration with Th. Fauster (Univ. Erlangen), M. Rohlfing (U Bremen)

UP3: Spin-polarized image-potential-state electrons as ultrafast magnetic sensors in front of ferromagnetic surfaces (DFG WE2037/1-2), in collaboration with M. Donath (Univ. Münster) (DFG DO502/4-2)

UP4: Dynamics at liquid water surfaces studied by laser pump – synchrotron-radiation probe experiments, in collaboration with M. Faubel (MPI Göttingen), P. Jungwirth (Univ. Prague), and C. Pettenkofer (HMI Berlin)

UP5: Studies of free and levitated nano-particles using synchrotron and FEL radiation, in collaboration with E. Rühl (Univ. Würzburg), Th. Leisner (TU Ilmenau), U. Becker (Fritz-Haber-Institut, Berlin), W. Widdra (Univ. Halle), D. Gerlich (TU-Chemnitz)

UP6: Material structuring with femtosecond technology, (DFG Ro 2074/5-1), International Office of the DFG (WTZ program with the Institute of Thermophysics, Novosibirsk, Russia)

3. Results in 2004

UP1: Collective excitations at semiconductor surfaces. A time-resolution of about 10 ps is demonstrated at the MBI - BESSY beamline in the so-called low-α mode of the Berlin synchrotron facility. This result implies an even better synchronization between femtosecond laser and synchrotron-radiation pulses. Relocating the experiment to a new beamline in early 2004 allows now to match foci of synchrotron and laser radiation to below 50 µm, which, together with the electronic gating of the detector, turned out to be essential requirements to record data with sufficient resolution and statistics in the BESSY hybrid mode.

UP2: Dynamics at Si(100). The electronic structure and electron dynamics at the Si(100) surface was studied by two-photon photoemission with femtosecond laser pulses.
At a temperature of 90 K the occupied Dup dangling bond state is located 150±30 meV below the valence band maximum (VBM) at the center of the surface Brillouin zone Γ and exhibits an effective hole mass of 0.5±0.15 me. The unoccupied D Down band has a local minimum at Γ of 650±30 meV above the VBM and shows strong dispersion along the dimer rows of the c(4 x 2) reconstructed surface.

2PPE spectra of Si(100) are dominated by interband transitions between the occupied and unoccupied surface states and emission out of transiently and permanently charged surface defects. Including electron-hole interaction in many-body calculations of the quasi-particle band structure leads us to assign a dangling bond split-off state to a quasi-one-dimensional surface exciton with a binding energy of 130 meV. Electrons resonantly excited to the unoccupied D Down dangling-bond band with an excess energy of about 350 meV need 1.5 ps to scatter via phonon emission to the band bottom at Γ and relax within 5 ps with an excited hole in the occupied surface band to form the exciton living for nanoseconds [WKS, FWe].

UP3: Spin-polarized image-potential-state electrons as ultrafast magnetic sensors in front of ferromagnetic surfaces. The interactions between water molecules and dissolved ions are of crucial importance for many physical and chemical processes. Specifically, enhanced anion concentrations at the salt solution interface play an important role in various atmospheric and environmental chemical processes. The present VUV photoemission study is concerned with iodide's large propensity for the solution surface. In the experiment iodide was added to aqueous tetrabutylammonium-bromide (TBABr) solution, with the iodide concentration.

At a temperature of 90 K the occupied Dup dangling bond state is located 150±30 meV below the valence band maximum (VBM) at the center of the surface Brillouin zone Γ and exhibits an effective hole mass of 0.5±0.15 me. The unoccupied D Down band has a local minimum at Γ of 650±30 meV above the VBM and shows strong dispersion along the dimer rows of the c(4 x 2) reconstructed surface.

2PPE spectra of Si(100) are dominated by interband transitions between the occupied and unoccupied surface states and emission out of transiently and permanently charged surface defects. Including electron-hole interaction in many-body calculations of the quasi-particle band structure leads us to assign a dangling bond split-off state to a quasi-one-dimensional surface exciton with a binding energy of 130 meV. Electrons resonantly excited to the unoccupied D Down dangling-bond band with an excess energy of about 350 meV need 1.5 ps to scatter via phonon emission to the band bottom at Γ and relax within 5 ps with an excited hole in the occupied surface band to form the exciton living for nanoseconds [WKS, FWe].

UP3: Spin-polarized image-potential-state electrons as ultrafast magnetic sensors in front of ferromagnetic surfaces. The interactions between water molecules and dissolved ions are of crucial importance for many physical and chemical processes. Specifically, enhanced anion concentrations at the salt solution interface play an important role in various atmospheric and environmental chemical processes. The present VUV photoemission study is concerned with iodide's large propensity for the solution surface. In the experiment iodide was added to aqueous tetrabutylammonium-bromide (TBABr) solution, with the iodide concentration.

2PPE spectra of Si(100) are dominated by interband transitions between the occupied and unoccupied surface states and emission out of transiently and permanently charged surface defects. Including electron-hole interaction in many-body calculations of the quasi-particle band structure leads us to assign a dangling bond split-off state to a quasi-one-dimensional surface exciton with a binding energy of 130 meV. Electrons resonantly excited to the unoccupied D Down dangling-bond band with an excess energy of about 350 meV need 1.5 ps to scatter via phonon emission to the band bottom at Γ and relax within 5 ps with an excited hole in the occupied surface band to form the exciton living for nanoseconds [WKS, FWe].

UP3: Spin-polarized image-potential-state electrons as ultrafast magnetic sensors in front of ferromagnetic surfaces. The interactions between water molecules and dissolved ions are of crucial importance for many physical and chemical processes. Specifically, enhanced anion concentrations at the salt solution interface play an important role in various atmospheric and environmental chemical processes. The present VUV photoemission study is concerned with iodide's large propensity for the solution surface. In the experiment iodide was added to aqueous tetrabutylammonium-bromide (TBABr) solution, with the iodide concentration.

UP4: Liquid jet studies. The interactions between water molecules and dissolved ions are of crucial importance for many physical and chemical processes. Specifically, enhanced anion concentrations at the salt solution interface play an important role in various atmospheric and environmental chemical processes. The present VUV photoemission study is concerned with iodide's large propensity for the solution surface. In the experiment iodide was added to aqueous tetrabutylammonium-bromide (TBABr) solution, with the iodide concentration.
anions being in great excess over the bromide anions. Supported by molecular dynamics (MD) simulations iodide is found to be more enhanced in the interfacial layer, covered by surface-active tetrabutyl-ammonium cations, as compared to bromide.

The cations are surface-bound due to hydrophobic interactions of the butyl chains, while the anions exhibit a propensity for the vacuum/solution interface due to their appreciable polarizability and size, which are both larger for iodide than from bromide. This anion specificity also explains the experimentally observed lower activity of TBABr compared to TBAI in polar solvents [WWW04, WWS04a, WWS04b].

**UP5: Studies of free and levitated nanoparticles using synchrotron and FEL radiation.** In this subproject we study single isolated nanoparticles when they are exposed to VUV and soft X-ray synchrotron radiation. The key component for experiments on isolated nanoparticles or micro-particles is a quadrupole particle trap. It consists of electrodes, where suitable AC- and DC-voltages are applied to stabilize the charged particle in the center of the trap. Any change in mass or charge state leads to changes in the motion frequencies of the trapped particle. These are monitored by an optical detection system, which also serves to characterize the charge-to-mass ratio of the particle. The detectable changes of the charge state can be as low as one elementary charge [GLS04]. From such charging experiments one can derive fundamental processes that can only occur in isolated matter, e.g. in chemically tailored nano-particles.

**UP6: Material structuring with femtosecond technology.** Dynamic pulse temporal tailoring and adaptive optimization open up opportunities to regulate and manipulate excitation of the electronic system and energy transfer. This allows to exploit dynamic processes and to optimize structuring.

Sequential energy delivery induces a stepwise preparation of the material, influences the balance between the induced non-thermal and thermal mechanisms for particle ejection, and if feedback-assisted provides a material specific optimization process. We propose a procedure based on evolutionary algorithms using phase modulation and subsequent temporal pulse tailoring to improve the characteristics of a Si ion beam emitted from laser irradiated silicon targets at moderate fluences [SMW04, SMS]. By optimizing the energy delivery rate impinging on the silicon target we can take advantage of a succession of phase transformations, drive the system in specific thermodynamic states, and obtain controllable low-kinetic-energy and high-flux ion beams for practical purposes, among them ion implantation in micro- and optoelectronics (Fig. 6). A theoretical study was performed on the role of rapid electronic transport in defining the characteristics of material removal with ultra-short laser pulses. The developed models are general and can be used to describe charge transport dynamics in different materials on ultra-fast timescales [BSR04a,b].

**Fig. 4b:** Typical snapshot from MD simulations of 16 TBAI ion pairs in a slab containing 16 NaBr ion pairs and 863 water molecules (31×31×30 Å³). Color coding: TBA⁺ - light blue and white, iodide – magenta, bromide – gold, sodium – green, water – red and white sticks. Already from the snapshot the segregation patterns of the ions in the interfacial layer can be seen qualitatively.

**Fig. 6:** (a) Evolution of the Si⁺ ion yield during the optimization run. A ten fold increase is obtained for the ion yield with a velocity of 4.5x10⁴ m/s at a fluence of 0.9 J/cm². (b) TOF mass-resolved Si⁺ trace corresponding to the single pulse and optimal pulse respectively. (c) Temporal intensity envelope of the optimal pulse.

**Fig. 5:** Electron emission distributions for single 84 eV photon absorption of SiO₂ nano-particle with and without a 39 nm gold shell. The probabilities are modeled by Poisson distributions and they show a significant difference between gold coated and plain silica.