submitted

Deterministic control of nanooptical excitations in plasmonic nanostructures using ultrashort polarization-shaped laser pulses
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, S. Cunovic, A. Fischer, P. Melchior, W. Pfeiffer, M. Rohmer, C. Schneider, C. Strüber, P. Tuchscherer, D. V. Voronine;

Optimal open-loop control, i.e. the application of an analytically derived control rule, is demonstrated for nanooptical excitations using polarization-shaped laser pulses. Optimal spatial nearfield localization in gold nanoprisms and excitation switching is realized by applying a π shift to the relative phase of the two polarization components. The achieved near-field switching confirms theoretical predictions, proves the applicability of predefined control rules in nanooptical light-matter interaction, and reveals local mode interference as an important control mechanism.

Time-resolved X-ray photoelectron spectroscopy at FLASH
S. Hellmann, C. Sohrt, M. Beye, T. Rohwer, F. Sorgenfrei, M. Marczynski-Bühlow, M. Kalläne, H. Redlin, F. Hennies, M. Bauer, A. Föhlisch, L. Kipp W. Wurth, K. Rossnagel;
The technique of time-resolved pump-probe X-ray photoelectron spectroscopy using the free-electron laser in Hamburg, FLASH, is described in detail. Particular foci lie on the macrobunch resolving detection scheme, the role of vacuum space-charge effects, and the synchronization of pump and probe lasers. In an exemplary case study, the complete Ta 4f core-level dynamics in the layered charge-density-wave compound 1T–TaS2 in response to impulsive optical excitation is measured on the sub-picosecond to nanosecond timescale. The observed multicomponent dynamics is related to the intrinsic melting and reformation of the chargedensity wave as well as to extrinsic pump-laser induced vacuum space-charge effects.

Reversible Switching in Self-assembled Monolayers of Azobenzene Thiolates on Au(111) Probed by Threshold Photoemission
N. Heinemann, J. Grunau, T. Leißner, O. Andreyev, S. Kuhn, U. Jung, D. Zargarani, R. Herges, O. Magnussen, M. Bauer;

The reversible photo- and thermally activated isomerization of the molecular switch 3-(4-(4-Hexyl-phenylazo)-phenoxy)-propane-1-thiol (ABT)1 deposited by liquid phase self-assembly on Au (111) (ABT/Au) was studied using laser-based photoelectron spectroscopy. Differences in the molecular dipole moment characteristic for the trans and cis isomer of ABT are monitored via changes in the sample work function accessible by detection of the threshold energy for photoemission. A quantitative analysis of our data shows that the fraction of molecules within the densely packed monolayer that undergoes a switching process is of the order of 1 %. This result indicates the relevance of substrate and/or film defects required to overcome the steric and/or electronic hindrance of the isomerisation reaction in a densely packed monolayer.

Probing the switching state of a surface-mounted azobenzene derivative using femtosecond XUV photoemission
J. Grunau, N. Heinemann, T. Rohwer, D. Zargarani, S. Kuhn, U. Jung, L. Kipp, O. Magnussen, R. Herges, M. Bauer;

Photoemission spectroscopy using femtosecond XUV light pulses is applied to probe the isomerization state of the molecular switch 3-(4-(4-hexyl-phenylazo)-phenoxy)-propane-1-thiol deposited by liquid phase self-assembly on Au(111). Spectral shifts of valence-electronic signatures that we associate with the carbon C2s orbital enable us to distinguish the trans and the cis isomerization state of the adsorbed molecules. These preliminary results envision the potential to probe reversible switching processes of surface-mounted molecules in real time by tracking the temporal evolution of the electronic and nuclear degrees of freedom in a femtosecond XUV photoemission experiment.

2011

Collapse of long-range charge order tracked by time-resolved photoemission at high momenta
T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohrt, A. Stange, B. Slomski, A. Carr, Y. Liu, L. Miaja Avila, M. Kalläne, S. Mathias, L. Kipp, K. Rossnagel, M. Bauer; Nature 471, (2011) 490

In condensed matter systems, intense femtosecond light pulses can transform electronic, magnetic and structural order on the fundamental timescales of electronic and atomic motion. This phenomenon is particularly attractive in the study and in the controli of materials whose physical properties are governed by the interactions between multiple degrees of freedom. Time- and angle-resolved photoemission spectroscopy is in this context the potentially most direct and comprehensive, energy- and momentum-selective probe of the ultrafast processes that couple to the electronic degrees of freedom. Previously, the capability of such studies to access electron momentum space further away from zero momentum was, however, restricted due to limitations of the available probing photon energy. Here, employing femtosecond extreme ultraviolet pulses delivered by a high-harmonic-generation source, we use time- and angle-resolved photoemission spectroscopy to measure the photo-induced vaporisation of a charge-ordered state in the potential excitonic insulator 1T-TiSe2. Via stroboscopic imaging of electronic band dispersions at large momentum, in the vicinity of the edge of the first Brillouin zone, we reveal that the collapse of atomic-scale periodic long-range order happens on a timescale as short as 20 femtoseconds. The surprisingly fast response of the system is assigned to screening by the transient generation of free charge carriers. Similar screening scenarios will likely be relevant in other photo-induced solid-state transitions and may generally determine the response times. Moreover, since electron states with large momenta govern fundamental electronic properties in condensed matter systemsii, we anticipate that the experimental advance represented by the present study will allow novel insights into the ultrafast dynamics and microscopic mechanisms of electronic phenomena in a wide range of materials.

CDW-superlattice suppression probed in time-resolved XUV-photoemission at the border of the Brillouin zone
T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohrt, A. Stange, B. Slomski, M. Kalläne, S. Mathias, L. Kipp, K. Rossnagel, M. Bauer; In "Ultrafast Phenomena XVII", Oxford University Press, Inc. (2011) 161

Deterministic Control in Subwavelength Field Localization in Plasmonic Nanoantennas
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, S. Cunovic, A. Fischer, P. Melchior, W. Pfeiffer, M. Rohmer, C. Schneider, C. Strüber, P. Tuchscherer, D. V. Voronine; In "Ultrafast Phenomena XVII", Oxford University Press, Inc. (2011) 667

Two-Photon Photoemission from ex-situ prepared Butanethiol SAMs on Au(111)
N. Heinemann, T. Leissner, J. Grunau, T. Rohwer, O. Andreev, M. Bauer; Chemical Physics 382 (2011) 1

Self-assembled monolayers (SAMs) of butanethiol on a Au(111) single crystalline surface in the p× √3 lying-down phase prepared by deposition from solution were studied with two-photon photoemission (2PPE) spectroscopy. The spectra reveal clear signatures of two unoccupied resonance states at energies E-EF = 3.7 eV and 3.9 eV. The low-energy state is assigned to the characteristic σ*-resonance associated with the Au-S bond of the thiolate. The energy of the other resonance state agrees well with an interface state reported before for different alkanethiol SAMs on Au(111) in a standing-up phase. The 2PPE data provide furthermore indications that the high quality of the ex-situ prepared SAMs support the formation of image potential states.

Surface plasmon polariton emission prompted by organic nanofibers on thin gold films
T. Leissner, K. Thilsing-Hansen, C. Lemke, S. Jauernik, J. Kjelstrup-Hansen, M. Bauer, H. -G. Rubahn; Plasmonics, DOI: 10.1007/s11468-011-9301-9

The excitation of surface plasmon polaritons (SPP) at a gold-vacuum interface by femtosecond light-pulses mediated by organic nanofiber-induced dielectric perturbations is observed using interferometric time-resolved photoemission electron microscopy (ITR-PEEM). The experimental data are quantitatively reproduced by analytic simulations, where the nanofibers are considered as superior source of the SPP emission. The flexibility and tuneability of phenylene-based nanofibers in their morphology and intrinsic optical properties open up future applications to fabricate custom-designed nanoscale sources of SPP's.

2010

Ultrafast melting of a charge-density wave probed on the atomic scale
S. Hellmann, M. Beye, C. Sohrt, T. Rohwer, F. Sorgenfrei, H. Redlin, M. Kalläne, M. Marczynski-Bühlow, M. Bauer, A. Föhlisch, L. Kipp, W. Wurth , K. Rossnagel; Phys. Rev. Lett. 105 (2010) 187401

Femtosecond time-resolved core-level photoemission spectroscopy with a free-electron laser is used to measure the atomic-site specific charge-order dynamics in the charge-density-wave/Mott insulator 1T-TaS2. After strong photoexcitation, a prompt loss of charge order and subsequent fast equilibration dynamics of the electron-lattice system are observed. On the time scale of electron-phonon thermalization, about 1 ps, the system is driven across a phase transition from a long-range charge ordered state to a quasi-equilibrium state with domain-like short-range charge order. The experiment opens the way to study the nonequilibrium dynamics of condensed matter systems with full elemental, chemical, and atomic site selectivity.

Probing adsorbate dynamics with chirped laser pulses in a single pulse scheme
F. Steeb, S. Mathias, M. Wiesenmayer, A. Fischer, M. Aeschlimann, M. Bauer, J. P. Gauyacq; Phys. Rev. B 82 (2010) 165430

Femtosecond dynamics of the model-like adsorption system Cs/Cu(111) is probed by two-photon photoelectron spectroscopy (2PPE) using phase-modulated (chirped) laser pulses. The experimental data are quantitatively modeled within a wavepacket propagation approach under explicit consideration of the adsorbate motion. The results enable us to assign characteristic chirped-pulse 2PPE features to the ultrafast adsorbate dynamics associated with the excited state lifetime and the adsorbate motion and to improve on the qualitative interpretation of experimental data as published in reference []. Our results show that non-linear photoemission with a chirped pulse in a single-pulse scheme can complement real-time studies based on pump-probe schemes to gain quantitative insights into the femtosecond dynamics of ultrafast surface processes.

Spatiotemporal control of nanooptical excitations
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, S. Cunovic, F. Dimler, A. Fischer, W. Pfeiffer, M. Rohmer, C. Schneider, F. Steeb, C. Strüber, D. V. Voronine; Proc. Natl. Acad. Sci. 107, 5329 (2010)

The most general investigation and exploitation of light-induced processes require simultaneous control over spatial and temporal properties of the electromagnetic field on a femtosecond time and nanometer length scale. Based on the combination of polarization pulse shaping and time-resolved two-photon photoemission electron microscopy, we demonstrate such control over nanoscale spatial and ultrafast temporal degrees of freedom of an electromagnetic excitation in the vicinity of a nanostructure. The time-resolved cross-correlation measurement of the local photoemission yield reveals the switching of the nanolocalized optical near-field distribution with a lateral resolution well below the diffraction limit and a temporal resolution on the femtosecond time scale. In addition, successful adaptive spatiotemporal control demonstrates the flexibility of the method. This flexible simultaneous control of temporal and spatial properties of nanophotonic excitations opens new possibilities to tailor and optimize the light– matter interaction in spectroscopic methods as well as in nanophotonic applications.

Quantum-Well-Induced Giant Spin-Orbit Splitting
S. Mathias, A. Ruffing, F. Deicke, M. Wiesenmayer, I. Sakar, G. Bihlmayer, E. . Chulkov, Yu. M. Koroteev, P. M. Echenique, M. Bauer, M. Aeschlimann; Phys. Rev. Lett. 104 (2010) 066802

We report on the observation of a giant spin-orbit splitting of quantum-well states in the unoccupied electronic structure of a Bi monolayer on Cu(111). Up to now, Rashba-type splittings of this size have been reported exclusively for surface states in a partial band gap. With these quantum-well states we have experimentally identified a second class of states that show a huge spin-orbit splitting. First-principles electronic structure calculations show that the origin of the spin-orbit splitting is due to the perpendicular potential at the surface and interface of the ultrathin Bi film. This finding allows for the direct possibility to tailor spin-orbit splitting by means of thin-film nanofabrication.

Time-resolved photoelectron spectroscopy at surfaces using femtosecond XUV-pulses
S. Mathias, M. Bauer, M. Aeschlimann, L. Miaja-Avila, H. C. Kapteyn, M. M. Murnane; book contribution, in production [Abstract]

Ultrashort XUV pulses from laser-based high-harmonic sources and free-electron lasers are an exceptional and promising tool for monitoring ultrafast dynamical processes at surfaces. In this contribution, we review recent progress in time-resolved photoelectron spectroscopy studies of surfaces that employ these light sources, with particular emphasis on technical aspects, pioneering experiments, and future perspectives.

Two-Photon Photoemission of Plasmonic Nanostructures with High Temporal and Lateral Resolution
M. Bauer, D. Bayer, C. Wiemann, M. Aeschlimann; in 'Nonlinear Dynamics of Nanosystems', Eds.: Radons, Rumpf, Schuster, Whiley-VCH, Weinheim (2010)

In this contribution we illustrate the potential of the time-resolved two-photon photoemission technique (TR-2PPE) to study static and dynamic properties of localized surface plasmons (LSP) in silver nanoparticles. In a first example, we show that conventional (laterally integrating) TR-2PPE is a highly sensitive tool for the detection of LSP resonances in metallic nanoparticles. This technique enables us to address the LSP induced enhancement of the local electric field as well as the decay dynamics of the LSP excitation. Studies at a lateral resolution well below the optical diffraction limit were performed with a detection scheme combining the time-resolved two-photon photoemission and the photoemission electron microscopy (PEEM). Operated at a typical resolution in the sub-30 nm regime, this technique enables systematic studies of the local dynamics associated with the excitation of single nanoparticles. Experimental examples include the real-time observation of the retardation of the LSP mode across a single nanoparticles and the coupling between neighbouring nanoparticles induced by the dipolar field associated with the LSP excitation.

Band structure dependence of hot-electron lifetimes in a Pb/Cu(111) quantum-well system
S. Mathias, A. Ruffing, F. Deicke, M. Wiesenmayer, M. Aeschlimann, M. Bauer; Phys. Rev. B 81, 15542 (2010) [Abstract]

The band-structure dependence of the inelastic lifetime of electrons is investigated in a Pb quantum-well system on a Cu(111) substrate with femtosecond time- and angle-resolved two-photon photoemission. For a single monolayer of Pb on Cu(111), we find an unoccupied quantum-well state with a free-electronlike parabolic dispersion around the 􀀀-point, and with negative dispersion for finite momentum. Our investigation of this state is the first momentum-resolved study of lifetimes in a quantum-well system. We demonstrate the importance of intrasubband-scattering processes for the decay of hot electrons at finite momentum. Furthermore, we find that the competition between intersubband- and intrasubband-scattering processes directly induces a momentum anisotropy in the hot-electron lifetimes. This momentum anisotropy is strongly dependent on the specific electronic band dispersion. We compare our findings with previous investigations of ultrafast electron dynamics in model-like surface-state systems and with ultrafast electron dynamics in Pb full-bulk material. Our findings suggest that the peculiar electronic structure of quantum-well systems can be used to tune ultrafast dynamical properties in metals.

Time-resolved photoelectron nano-spectroscopy of individual silver particles: perspectives and limitations
M. Rohmer, M. Bauer, T. Leissner, Ch. Schneider, A. Fischer, G. Niedner-Schatteburg, B. v. Issendorff, M. Aeschlimann; Phys. Stat. Sol. (b) 247 (2010) 1133 [Abstract]

Simultaneous time- and energy-resolved two-photon photoemission with nanometer resolution is demonstrated for the first time. We monitor the energy dependence of the decay dynamics of electron excitations in individual silver particles, which were deposited from a gas aggregation cluster source onto a silicon substrate. We show furthermore that the near-field enhancement due to plasmon-resonant excitation is an efficient means to address individual nanometer sized particles using

Photoemission Electron Microscopy.

Spectroscopy and population decay of a Ti excess state in layered TiSe2
M. Wiesenmayer, S. Hilgenfeldt, S. Mathias, F. Steeb, T. Rohwer, M. Bauer; Phys. Rev. B 82 (2010) 035422 [Abstract]

Two-photon photoelemission (2PPE) spectroscopy is used to map the momentum dependent energy distribution of electronic excitations in the layered 1T-TiSe2 transition metal dichalcogenide compound. A comparison of the experimental results with previous calculations based on the local density functional approach enables us to identify the second Ti 3d conduction band and a localized excitation state arising from the presence of excess titanium atoms in the van der Waals gap of the crystal. Time-resolved 2PPE measurements show clear differences in the lifetime between the two states, indicative for the decoupling of the Ti excess atoms from the bulk electronic structure.

2009

Quantum oscillations in coupled two-dimensional electron systems
S. Mathias, S. V. Eremeev, E. V. Chulkov, M. Aeschlimann, M. Bauer; Phys. Rev. Lett. 103 (2009) 026802

Quantum oscillations of the electron phonon coupling of a Shockley surface state induced by the coupling to a metallic quantum well are observed experimentally as the thickness of the quantum well is increased. Microscopic calculations allow us to assign these oscillations to changes in the Eliashberg function, which are caused by a modulation in the wavefunction overlap between the 2D surface state band and the 2D electron system of the quantum well. The findings are important in the context of the control of surface processes such as film growth and surface chemical reactions.

The nature of a nonlinear excitation pathway from the Shockley surface state as probed by chirped pulse two photon photoemission
F. Steeb, S. Mathias, A. Fischer, M. Wiesenmayer, M. Aeschlimann, M. Bauer; New Journal of Physics 11 (2009) 013016

Phase-modulated femtosecond laser pulses are used to study the spectral response of a non-resonant two photon excitation from the Cu(111) Shockley surface state. Controlled variations in the spectral phase of the laser pulse were introduced using a tuneable Fork prism phase modulator and resulted in a shift in the peak-position (of up to 110 meV), variations in the spectral width (up to 88 meV) and changes in the asymmetry of the surface state peak as detected by two-photon photoemission. A satisfactory quantitative model of the experimental results can only be achieved if the complete spectral phase up to the third order dispersion terms is taken into account. Of particular note, we find that a consistent description of this two photon absorption process does not require coupling of the excitation to an intermediate copper bulk state, which contradicts the previous results of Petek and coworkers [1].

[1] Petek H, Heberle A P, Nessler W, Nagano H, Kubota S, Matsunami S, Moriya N and Ogawa S 1997 Phys. Rev. Lett. 79 4649

Determination of spin injection and transport in a ferromagnet/organic semiconductor heterojunction by two-photon photoemission
M. Cinchetti, K. Heimer, J. -P. Wüstenberg, O. Andreyev, M. Bauer, S. Lach, C. Ziegler, Y. Gao, M. Aeschlimann; Nature Materials, 8 (2009) 115

A fundamental prerequisite for the implementation of organic semiconductors (OSCs) in spintronics devices is the still missing basic knowledge about spin injection and transport in OSCs. Here, we consider a model system consisting of a high-quality interface between the ferromagnet cobalt and the OSC copper phthalocyanine (CuPc). We focus on interfacial effects on spin injection and on the spin transport properties of CuPc. Using spin-resolved two-photon photoemission, we have measured directly and in situ the efficiency of spin injection at the cobalt–CuPc interface. We report a spin injection efficiency of 85–90% for injection into unoccupied molecular orbitals of CuPc. Moreover, we estimate an electron inelastic mean free path in CuPc in the range of 1 nm and a 10–30 times higher quasi-elastic spin-flip length. We demonstrate that quasi-elastic spin-flip processes with energy loss less than or equal to200 meV are the dominant microscopic mechanism limiting the spin diffusion length in CuPc.

Time and angle resolved photoemission spectroscopy using femtosecond visible and high-harmonic light
S. Mathias, M. Wiesenmayer, F. Deicke, A. Ruffing, L. Miaja-Avila, M. M. Murnane, H. C. Kapteyn, M. Bauer, M. Aeschlimann; J. Phys.: Conference series 148 (2009) 012042

The angle resolved photoelectron spectroscopy (ARPES) has emerged as a leading technique in identifying static key properties of complex systems such as the electronic band structure of adsorbed molecules, ultrathin quantum-well films or high temperature superconductors. We efficiently combined

ARPES by using a two-dimensional analyzer for parallel energy (E) and momentum (k||) detection with femtosecond time-resolved spectroscopies. Using time and angle resolved two photon photoemission (2PPE) with visible light pulses, the hot electron dynamics in complex electronic structures are directly accessible by means of angle resolved hot electron lifetime mapping. Furthermore, femtosecond ARPES spectra recorded with high harmonic generation (HHG) light pulses are presented, showing the potential of this technique for future investigations of surface dynamics and photo-induced phase transition processes.

Simultaneous Spatial and Temporal Control of Nanooptical Fields
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, S. Cunovic, F. Dimler, A. Fischer, W. Pfeiffer, M. Rohmer, C. Schneider, F. Steeb, C. Strüber, D. V. Voronine; In "Ultrafast Phenomena XVI", Springer Series in Chemical Physics; In "Ultrafast Phenomena XVI", Springer Series in Chemical Physics, 705 (2009)

Using time-resolved two-photon photoemission electron microscopy we demonstrate simultaneous spatial and temporal control of nanooptical fields. Cross correlation measurements reveal the ultrafast spatial switching of the local excitation on a subdiffraction length scale.

Time and space resolved studies on metallic nanoparticles
D. Bayer, J. Lange, C. Wiemann, M. Rohmer, M. Bauer, M. Aeschlimann; In "Physics and Engineering of New Materials", p. 61, Eds. D.T. Cat, A. Pucci and K. Wandelt, Springer Proceedings in Physics 127 (2009)

The dynamics of laser-excited electronic excitations (localized surface plasmons) in spherical Ag nanoparticles is studied by phase and time resolved two photon photoemission (TR-2PPE) and photoelectron emission microscopy (TR-PEEM). A two-dimensional array of nearly identical, parallelly oriented particles is deposited lithographically on a transparent ITO covered glass substrate. We are able to show that the parallel acquisition mode of the PEEM enables us to resolve local variations in the ultrafast electron dynamics in the nanoparticles with an accuracy of 1fs and a lateral resolution in the nanometer regime. A qualitative interpretation of the mapped inhomogeneities in the local electron dynamics is provided.

2008

Direct measurement of core-level relaxation dynamics on a surface-adsorbate system
L. Miaja-Avila, G. Saathoff, S. Mathias, J. Yin, C. La-o-vorakiat, M. Bauer, M. Aeschlimann, M. M. Murnane, H. C. Kapteyn; Phys. Rev. Lett. 101 (2008) 046101

The coupling between electronic states of an adsorbate and the surface on which it resides is fundamental to the understanding of many surface interactions. In this work, we present the first direct time-resolved observations of the lifetime of core-excited states of an atom adsorbed onto a surface. By comparing laser-assisted photoemission from a substrate with a delayed Auger decay process from an adsorbate, we measure the lifetime of the 4d-1 core level of Xenon on Pt(111) to be 7.1 ± 1.1 fs. This result opens up time domain measurements of highly-excited state dynamics at surfaces where, because of complex interactions, energy-resolved measurements may provide incomplete information.

The lifetime of an adsorbate excitation modified by a tuneable two-dimensional substrate
M. Wiesenmayer, M. Bauer, S. Mathias, M. Wessendorf, E. V. Chulkov, V. M. Silkin, A. G. Borisov, J.-P. Gauyacq, P. M. Echenique, M. Aeschlimann; Phys. Rev. B 78, 245410 (2008)

The coupling efficiency between an adsorbate and a two-dimensional substrate is probed by real-time monitoring of the ultrafast charge transfer between a Cs atom and an ultrathin silver film of varying thickness adsorbed on a Cu(111) surface. For the first two monolayers of the silver film, a reduction in the resonance lifetime of the cesium 6s-6p hybrid state of approximately 35% is observed. When the silver coverage further increases, the resonance lifetime stays constant at a value close to the value for Cs adsorption on a bulk Ag(111) surface. Both the one-electron resonant and the multielectron inelastic contributions to the adsorbate-substrate charge transfer are theoretically evaluated based on wave-packet propagation and GW approximation. The results support the experimental findings and allow us to assign the observed dependence of the lifetime change in the multielectron inelastic contribution to the electron transfer rate between the Cs resonance and the very top atomic layers of the substrate.

Electron emission from films of Ag and Au nanoparticles excited by a femtosecond pump-probe laser
A. Gloskovskii, D. A. Valdaitsev, M. Cinchetti, S. A. Nepijko, J. Lange, M. Aeschlimann, M. Bauer, M. Klimenkov, L. V. Viduta, P. M. Tomchuk , G. Schönhense; Phys. Rev B 77 (2008) 195427

Electron emission from Ag and Au nanoparticle films was studied under excitation with femtosecond-laser pulses with photon energies of 1.55 and 3.1 eV. Films were grown on a glass substrate with particle sizes from the nanometer range to a continuous layer. The transition from a continuous film to a nanoparticle film is accompanied by an increase in photoemission current by more than an order of magnitude. Pump-and-probe experiments with variable delay gave information on the lifetime of the intermediate states. At a fixed pulse power, the emission yield increases as the temporal width of the laser pulses is decreased. Experimental results are interpreted in terms of two different electron emission mechanisms, i.e., multiphoton photoemission and thermionic emission or thermally assisted multiphoton photoemission. The first mechanism prevails for continuous films and larger particles with sizes above several tens of nanometers; the second one prevails for smaller nanoparticles with sizes of a few nanometers.

Spin injection and spin dynamics at the CuPc/GaAs interface studied with ultraviolet photoemission spectroscopy and two-photon photoemission spectroscopy
H. J. Ding, Y. L. Gao, M- Cinchetti, J. P. Wustenberg JP, M. Sanchez-Albaneda, O. Andreyev, M. Bauer, M. Aeschlimann; Phys. Rev. B 78 (2008) 075311

Interface formation between p-type GaAs(100) and the organic semiconductor copper phthalocyanine (CuPc) has been studied with ultraviolet photoemission spectroscopy and two-photon photoemission spectroscopy (2PPE). Spin-resolved 2PPE measurements show a highly efficient spin injection of hot electrons from GaAs into CuPc, demonstrating that spin-polarized electrons originating from the GaAs

substrate can be injected into CuPc without any substantial spin-flip scattering at the interface. Furthermore, spin- and time-resolved 2PPE measurements are employed to study the temporal evolution of the spin polarization injected into the organic layer in the range up to 1 ps after injection from the GaAs substrate. The results show that the degree of spin polarization of electrons injected through the GaAs/CuPc interface into molecular orbitals just above the lowest unoccupied molecular orbital onset of CuPc is preserved longer than the spin polarization of electrons injected in energetically higher lying states.

Dynamics of the coercivity in ultrafast pump–probe experiments
T. Roth, D. Steil, D. Hoffmann, M. Bauer, M. Cinchetti, M. Aeschlimann; J. Phys. D: Appl. Phys. 41 (2008) 164001

In this paper we devote ourselves to the coercivity as a measured variable in femtosecond magnetism. We stress the fact that an all optical pump–probe technique is in general not suitable to gain access to the time-dependent behaviour of the coercivity, since the switching in a fixed external field is an irreversible process. We comment on the possible mechanisms leading to the observed reduction in the coercivity with increasing pump power and propose a potential solution to clarify the origin of such behaviour.

Time-resolved 2PPE and time-resolved PEEM as a probe of LSP's in silver nanoparticles
D. Bayer, C. Wiemann, O. Gaier, M. Bauer, M. Aeschlimann, Journal of Nanomaterials 2008 (2008) 249514

The time-resolved two-photon photoemission technique (TR-2PPE) has been applied to study static and dynamic properties of localized surface plasmons (LSP) in silver nanoparticles. Laterally integrated measurements show the difference between LSP excitation and non-resonant single electron-hole pair creation. Studies below the optical diffraction limit were performed with the detection method of time-resolved photoemission electron microscopy (TR-PEEM). This microscopy technique with a resolution down to 40nm enables a systematic study of retardation effects across single nanoparticles. In addition, as will be shown in this paper, it is a highly sensitive sensor for coupling effects between nanoparticles.

Hot-electron dynamics in thin films of sodium-doped perylene-3,4,9,10-tetracarboxylic dianhydride
J. Wüsten, S. Berger, M. Salomo, A. Mönnich, M. Bauer, M. Aeschlimann, Ch. Ziegler; ; Phys. Rev. B 78, 195326 (2008)

Time resolved 2 photon photoemission (2PPE) measurements of the doping process of perylene-3,4,9,10-tetracarboxylicdianhydride (PTCDA) thin films with sodium give insight into the dynamics of hot electrons in this system. Interaction with sodium results in a charge transfer from sodium to PTCDA (”n-doping”) and is accompanied by an increase of the lifetime of electrons excited to unoccupied states 1.2 - 1.8 eV above the Fermi level. This result can be considered from two physical viewpoints, the one-electron picture, treated in ”classical” photoemission spectroscopy theory, and the many-electron excitations as commonly considered in optical spectroscopy. As thin PTCDA layers on a Ag(111) surface show up similar features in ultraviolet spectroscopy as sodium doped PTCDA, this system also was investigated by 2PPE. An increase of lifetime can be observed for thin PTCDA coverages.

Direct Measurement of Core-Level Relaxation Dynamics on a Surface-Adsorbate System using Ultrafast X-Rays
L. Miaja-Avila, G. Saathoff, S. Mathias, J. Yin, C. La-o-vorakiat, M. Bauer, M. Aeschlimann, M. M. Murnane, H. C. Kapteyn; 2008 Conference on Lasers and Electro-Optics & Quantum Electronics And Laser Science Conference, Vols. 1-9 Book Series: IEEE Lasers and Electro-Optics Society (LEOS) Annual Meeting, 3096-3097 (2008)

2007

Adaptive sub-wavelength control of nano-optical fields
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F. Javier Carcia de Abajo, W. Pfeiffer, M. Rohmer, Ch. Spindler, F. Steeb; Nature 446 (2007) 301

Adaptive shaping of the phase and amplitude of femtosecond laser pulses has been developed into an efficient tool for the directed manipulation of interference phenomena, thus providing coherent control over various quantum-mechanical systems. Temporal resolution in the femtosecond or even attosecond range has been demonstrated, but spatial resolution is limited by diffraction to approximately half the wavelength of the light field (that is, several hundred nanometres). Theory has indicated that the spatial limitation to coherent control can be overcome with the illumination of nanostructures: the spatial near-field distribution was shown to depend on the linear chirp of an irradiating laser pulse. An extension of this idea to adaptive control, combining multiparameter pulse shaping with a learning algorithm, demonstrated the generation of user-specified optical near-field distributions in an optimal and flexible fashion. Shaping of the polarization of the laser pulse provides a particularly efficient and versatile nano-optical manipulation method. Here we demonstrate the feasibility of this concept experimentally, by tailoring the optical near field in the vicinity of silver nanostructures through adaptive polarization shaping of femtosecond laser pulses and then probing the lateral field distribution by twophoton photoemission electron microscopy. In this combination of adaptive control and nano-optics, we achieve subwavelength dynamic localization of electromagnetic intensity on the nanometre scale and thus overcome the spatial restrictions of conventional optics. This experimental realization of theoretical suggestions opens a number of perspectives in coherent control, nano optics, nonlinear spectroscopy, and other research fields in which optical investigations are carried out with spatial or temporal resolution.

Adaptive Control of Nanoscopic Photoelectron Emission
M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F. J. García de Abajo, W. Pfeiffer, M. Rohmer, C. Spindler, F. Steeb; in Ultrafast Phenomena XV: Proceedings of the 15th International Conference, (2007) 633

We show experimentally that optimally polarization-shaped femtosecond laser pulses provide spatial control over electron photoemission from nanostructures. Emission patterns are manipulated with subdiffraction resolution, illustrating the potential of electric near-field control in nanophotonics.

Phase propagation of localized surface plasmons probed by time-resolved photoemission electron microscopy
M. Bauer, C. Wiemann, J. Lange, D. Bayer, M. Rohmer, M. Aeschlimann; Appl. Phys. A 88 (2007) 473

In combining time-resolved two-photon photoemission (TR-2PPE) and photoemission electron microscopy (PEEM) the ultra-fast dynamics of collective electron excitations
in silver nanoparticles (localized surface plasmons – LSPs) is probed at fs and nm resolution. Here we demonstrate that the sampling of the LSP dynamics by means of time-resolved PEEM enables detailed insight into the propagation processes
associated with these excitations. In phase-integrated as well as phase-resolved measurements we observe spatio-temporal modulations in the photoemission yield from a single nanoparticle. These modulations are assigned to local variations in the
electric near field as a result of the phase propagation of a plasmonic excitation through the particle. Furthermore, the control of the phase between the fs pump and probe laser pulses used for these experiments can be utilized for an external manipulation of the nanoscale electric near-field distribution at these particles.

Excited states in the alkali/noble metal surface systems: A model system for the study of charge transfer dynamics at surfaces
J. P. Gauyacq, A. G. Borisov, M. Bauer; Progress in Surface Science 82 (2007) 244–292

The low coverage adsorption of alkalis on metal surfaces induces excited states localised on the adsorbate. In the case of noble metal substrates, these excited states can exhibit a very long lifetime, up to tens of fs in the Cs/Cu(111) system. We review recent experimental and theoretical investigations of alkalis adsorbed on noble metal surfaces, with emphasis on the characteristics of the alkaliinduced excited states, the origin of their long lifetimes, and the consequences for the adsorbate dynamics. The possibility of long-lived resonances in other adsorbate/substrate systems is also discussed.

Spin- and time-resolved photoemission studies of thin Co2FeSi Heusler alloy films
J. P. Wüstenberg, M. Cinchetti, M. Sánchez Albaneda, M. Bauer, M. Aeschlimann; J. Magn. Magn. Mat. 316 (2007) e411-e414

We have studied the possibly half metallic Co2FeSi full Heusler alloy by means of spin- and time-resolved photoemission spectroscopy. For excitation, the second and fourth harmonic of femtosecond Ti:sapphire lasers were used, with photon energies of 3.1 eV and 5.9 eV , respectively. We compare the dependence of the measured surface spin polarization on the particular photoemission mechanism, i.e. 1-photon-photoemission (1PPE) or 2-photon photoemission (2PPE). The observed differences in the spin polarization can be explained by a spin-dependent lifetime effect occurring in the 2-photon absorption process. The difference in escape depth of the two methods in this case suggests that the observed reduction of spin polarization (compared to the bulk) cannot be attributed just to the outermost surface layer but takes place at least 4 − 6 nm away from the surface.

Angle Resolved Photoemission Spectroscopy with a Femtosecond High Harmonic Light Source using a 2D Imaging Electron Analyzer
S. Mathias, L. Miaja-Avila, M. M. Murnane, H. Kapteyn, M. Aeschlimann, M. Bauer; Rev. Sci. Instr. 78 (2007) 083105

An experimental setup for time- and angle-resolved photoemission spectroscopy using a femtosecond 1 kHz high harmonic light source and a 2D electron analyzer for parallel energy and momentum detection is presented. A selection of the 27th harmonic (41.85eV) from the harmonic spectrum of the light source is achieved with a multilayer Mo/Si double mirror monochromator. The extinction efficiency of the monochromator in selecting this harmonic is shown to be better than 7:1, while the transmitted bandwidth of the selected harmonic is capable of supporting temporal pulse widths as short as 5 fs. The recorded E(k) photoelectron spectrum from a Cu(111) surface demonstrates an angular resolution of better than 0.6° (=0,03 Å-1 at Ekin,e- =36 eV). Used in a pump-probe configuration, the described experimental setup represents a powerful experimental tool for studying the femtosecond dynamics of ultrafast surface processes in real-time.

Local 2PPE-yield enhancement in a defined periodic silver nanodisc array
C. Wiemann, D. Bayer, M. Rohmer, M. Aeschlimann, M. Bauer; Surf. Sci. 601 (2007) 4714

Well-prepared periodic arrays of silver nanoparticles are investigated by means of linear and non-linear photoemission electron microscopy. The structures show homogeneous photoemission for UV excitation in the linear photoemission regime whereas striking inhomogeneities are mapped in the case of the nonlinear (2 Photon) excitation using ultrashort 400 nm laser pulses. A detailed analysis enables to assign these inhomogeneities to defect induced electron momentum transfer processes only effective for the 2 photon excitation process. We propose this mechanism to be of relevance for the appearance of so-called hotspots in nonlinear photoemission as identified in other 2PPE studies in the past. Furthermore, the complementarity between all-optical studies and nonlinear photoemission studies of localized surface plasmons in nanoparticles is discussed.

Experimental time-resolved photoemission and ab initio GW+T study of lifetimes of excited electrons in ytterbium
A. Marienfeld, M. Cinchetti, M. Bauer, M. Aeschlimann, V. P. Zhukov, E. V. Chulkov, P. M. Echenique; J. Phys.: Condens. Matter 19 (2007) 496213

In this paper we give a detailed analysis of the difference between the
lifetimes of Yb quantum-well states measured by scanning tunnelling spectroscopy (STS) in [Phys.

Rev. Lett. 94, 126804 (2005)] and lifetimes of bulk Yb obtained by means of time-resolved two-photon photoemission spectroscopy (TR-2PPE). In particular, we show that in spite of a seeming disagreement with the TR-2PPE measurements, the inelastic lifetimes yielded in STS experiments are also close to the inelastic lifetimes of bulk states which emphasizes the complementarity of both methods. Our approach is supported by ab initio electron self-energy calculations performed within the GW and GW+T approximations. Moreover we analyze the impact of the 4f-states on the lifetimes. We show that the GW-term of the inverse lifetime (linewidth) is markedly less than the experimental linewidth. The agreement with experimental data is recovered when both electron-hole and electron-electron terms of the T-matrix are included in the linewidth calculations.

Mapping the femtosecond dynamics of supported clusters with nanometer resolution
M. Rohmer, F. Ghaleh, M. Aeschlimann, M. Bauer, H. Hövel; Eur. Phys. J. D 45, (2007) 491

In this paper we present a combined STM, SEM and time-resolved PEEM study of silver clusters on a nano-patterned HOPG-substrate, exhibiting areas of different defect type and defect densities. The areas show small but distinct differences in the femtosecond dynamics associated with electronic excitations in the clusters. We assign these differences to variations in the cluster size distribution and variations in the cluster-substrate interaction as governed by the bonding to the different defect types.

Excited electron dynamics in bulk ytterbium: Time-resolved two-photon photoemission and GW+T *ab initio* calculations
V. P. Zhukov, E. V. Chulkov, P. M. Echenique, A. Marienfeld, M. Bauer, M. Aeschlimann; Phys. Rev. B 76, 193107 (2007)

The excited electron dynamics in ytterbium is investigated by means of the time-resolved two-photon photoemission spectroscopy and ab initio GW+T-matrix approach. We show that the standard GW approach with core 4f-orbitals fails to describe the experimental energy trend of the lifetimes. However, a fine agreement with the experimental data is achieved within GW+T-matrix approach when 4f-orbitals are included in a valence basis set. In contrast to previous STS data, we show that at small excitation energy the energy dependence of lifetimes strongly deviates from that for the free electron gas. We also argue that the e-ph coupling in Yb should be weak.

2006

Quantum-Well Wavefunction Localization and the Electron-Phonon Interaction in Thin Ag Nanofilms
S. Mathias, M. Wiesenmayer, M. Aeschlimann, M. Bauer; Phys. Rev. Lett. 97, (2006) 236809

The electron-phonon interaction in thin Ag-nanofilms epitaxially grown on Cu(111) is investigated by temperature-dependent and angle-resolved photoemission from silver quantum-well states. Clear oscillations in the electron-phonon coupling parameter as a function of the silver film thickness are observed. We relate these oscillations to a sudden wavefunction localization of quantum-well states within the silver film at distinct film thicknesses. This mechanism is different from other thin film systems where quantum oscillations are related to the Fermi-level crossing of quantum well states.

Energy-Resolved Electron-Spin Dynamics at Surfaces of p-Doped GaAs
H. C. Schneider, J. P. Wuestenberg, O. Andreyev, K. Hiebbner, L. Guo, J. Lange, L. Schreiber, B. Beschoten, M. Bauer, M. Aeschlimann; Phys. Rev. B 73, 081302(R) (2006)

Electron-spin relaxation at different surfaces of p-doped GaAs is investigated by means of spin, time, and energy-resolved two-photon photoemission. These results are contrasted with bulk results obtained by time-resolved Faraday rotation measurements as well as calculations of the Bir-Aronov-Pikus spin-flip mechanism. Due to the reduced hole density in the band bending region at the (100) surface the spin-relaxation time increases over two orders of magnitude towards lower energies. At the flat-band (011) surface a constant spin relaxation time in agreement with our measurements and calculations for bulk GaAs is obtained.

Space Charge Effects in Photoemission with a low repetition, high intensity femtosecond laser source
S. Passlack, S. Mathias, O. Andreyev, D. Mittnacht, M. Aeschlimann, M. Bauer; J. Appl. Phys. 100, (2006) 024912

In this paper, we present experimental results on the effect of space-charging in photoelectron spectroscopy from a surface using a pulsed and intense femtosecond light source. We particularly focus on a quantitative evaluation of the induced spectral broadening. Our results are compared with analytic calculations based on energy conservation considerations as well as with experimental results from measurements using picosecond pulses for the excitation process. As a measure of space charge effects, we monitored the angular and energy distribution of the photoemission from the occupied Shockley surface state of Cu(111) as a function of the total number N of the photoemitted electrons per laser pulse. Our results show that spectral distortions exist for the entire laser fluence regime probed. The energetic broadening of the surface state peak can be fitted with remarkable accuracy by a dependence, in agreement with the theoretical predictions and different from the experimental picosecond results, where a dominating linear dependence has been reported. In addition to a pure energetic broadening of the photoemission spectra, we also identify modifications in the angular distribution of the photoemitted electrons due to space charge effects.

Morphological Modifications of Ag/Cu(111) probed by Photoemission Spectroscopy of Quantum Well States and the Shockely Surface State
S. Mathias, M. Wessendorf, S. Passlack, M. Aeschlimann, M. Bauer; Appl. Phys. A 82 (2006) 439

Epitaxial ultra-thin Ag films grown on Cu(111) have been investigated by angle-resolved photoemission spectroscopy. The thickness dependence of the binding energy for the Shockley surface state at 300 K could be determined accurately in films up to 5 ML thick. Furthermore, we observe drastic changes in the film morphology after annealing to 450 K. Spectral modifications in the shape of the quantum-well states (QWS), characteristic for these ultra-thin silver films, prove that the surface morphology is homogeneous. The photoemission spectra also indicate that the silver film bifurcates to form a film exhibiting two distinct film thicknesses. For all levels of silver coverage, we identify surface regions that are 2 ML thick, while the thickness of the remaining surface depends on

the amount of deposited silver. The almost purely Lorentzian line-shape of the spectral features corresponding to the two different surface regions show that both surface areas are atomically flat.

Local correlation of Photoemission Electron Microscopy and STM at a defined cluster substrate system
M. Rohmer, C. Wiemann, M. Munzinger, L. Guo, M. Aeschlimann, M. Bauer; Appl. Phys. A 82 (2006) 87

We describe a technique that enables photoelectron spectroscopy and STM imaging of supported clusters from identical surface areas of a size of a few m² at a lateral resolution in the low nanometer regime. In this way we are able to locally correlate properties regarding the electronic structure of the clusters and their topography. The use of a photoemission electron microscope (PEEM) allows one to probe the local distribution of the photoemission yield from the sample at a resolution down to 20 nm. An STM-tip is used to remove clusters from their position and set local, well-defined markers at the surface that are clearly visible in the PEEM images. These markers act as reference points to identify surface areas in the PEEM image that have formerly been imaged by an STM. The present accuracy of this local correlation technique is at least 300 nm. We propose a scheme to further improve this correlation so that in future experiments even selected single clusters, which have been characterized by STM, can be addressed by local photoelectron spectroscopy as well as local time-resolved photoelectron spectroscopy.

Probing femtosecond plasmon dynamics with nanometer resolution
J. Lange, D. Bayer, M. Rohmer, C. Wiemann, O. Gaier, M. Aeschlimann, M. Bauer; Proc. SPIE Vol. 6195, (2006) 61950Z

In combining time-resolved two-photon photoemission (TR-2PPE) and photoemission electron microscopy (PEEM) the ultrafast dynamics of collective electron excitations in silver nanoparticles (localized surface plasmons – LSP) is probed at femtosecond and nanometer resolution. In two examples we illustrate that a phase-resolved (interferometric) sampling of the LSP-dynamics enables detailed insight into dephasing and propagation processes associated with these excitations. For two close-lying silver nano-dots (diameter 200 nm) we are able to distinguish small particle to particle variations in the plasmon eigenfrequency, which typically give rise to inhomogeneous line-broadening of the plasmon resonance in lateral integrating frequency domain measurements. The observed spatio-temporal modulations in the photoemission yield from a single nanoparticle can be interpreted as local variation in the electric near-field and result from the phase propagation of the plasmon through the particle. Furthermore, we show that the control of the phase between the used femtosecond pump and probe laser pulses used for these experiments can be utilized for an external manipulation of the nanoscale electric near-field distribution at these particles.

Spin-resolved two-photon photoemission study of the surface resonance state on Co/Cu(001)
O. Andreyev, Yu. M. Koroteev, M. Sánchez Albaneda, M. Cinchetti, G. Bihlmayer, E. V. Chulkov, J. Lange, F. Steeb, M. Bauer, P. M. Echenique, S. Blügel, M. Aeschlimann; Phys. Rev. B 74 (2006) 195416

Bulk and surface states of a clean and Cs-doped surface of a Co film grown on Cu(001)have been studied by spin-resolved photoemission (SR-PE) and compared with band structure calculation results. One-photon (1PPE) and two-photon (2PPE) photoemission spectra from clean Co films are found to be dominated by a peak located at a binding energy of about 0.4 eV with respect to EF, which is assigned to the spin up 3d bulk state. Slight Cs-doping of a Co(001) surface shifts an image potential state in resonance with the sp-states of the conduction band. SR-2PPE study of the optically-induced electron population in such an image resonance reveals a strong dependence on the set polarization of the laser light. We are able to directly detect the spin polarization of electrons photoemitted from the image resonance state, which can be varied from highlypolarized (about bulk values) to almost unpolarized when tuning light polarization of the pump laser pulse from s to p.

Spin-Flip Processes and Ultrafast Magnetization Dynamics in Co: Unifying the Microscopic and Macroscopic View of Femtosecond Magnetism
M. Cinchetti M. Sánchez Albaneda, D. Hoffmann, T. Roth, J. -P. Wüstenberg, M. Krauß, O. Andreyev, H. C. Schneider, M. Bauer, M. Aeschlimann; Phys. Rev. Lett. 97 (2006) 177201

The femtosecond magnetization dynamics of a thin cobalt film excited with ultrashort laser pulses has been studied using two complementary pump-probe techniques, namely, spin-, energy-, and time-resolved photoemission and the time-resolved magneto-optical Kerr effect. Combining the two methods, it is possible to identify the microscopic electron spin-flip mechanisms responsible for the ultrafast macroscopic magnetization dynamics of the cobalt film. In particular, we show that electron-magnon excitation does not affect the overall magnetization even though it is an efficient spin-flip channel on the sub-200 fs time scale. Instead, we find experimental evidence for the relevance of Elliott-Yafet-type spin-flip processes for the ultrafast demagnetization taking place on a time scale of 300 fs.

Experimental time-resolved photoemission and ab initio study lifetimes of excited electrons in Mo and Rh

A. Mönnich, J. Lange, M. Bauer, M. Aeschlimann, I. A. Nechaev, V. P. Zhukov, P. M. Echenique, E. V. Chulkov; Phys. Rev. B 74 (2006) 035102

We have studied the relaxation dynamics of optically excited electrons in molybdenum and rhodium by means of time resolved two-photon photoemission spectroscopy (TR-2PPE) and ab initio electron self-energy calculations performed within the GW and GW + T approximations. Both theoretical approaches reproduce qualitatively the experimentally observed trends and differences in the lifetimes of excited electrons in molybdenum and rhodium. For excitation energies exceeding the Fermi energy by more than 1 eV, the GW +T theory yields lifetimes in quantitative agreement with the experimental results. As one of the relevant mechanisms causing different excited state lifetime in Mo and Rh we identify the occupation of the 4d bands. An increasing occupation of the 4d bands results in an efficient decrease of the lifetime even for rather small excitation energies of a few 100 meV.

2005

The lateral Photoemission Distribution from a defined Cluster/Substrate System as probed by Photoemission Electron Microscopy
M. Munzinger, C. Wiemann, M. Rohmer, L. Guo, M. Aeschlimann, M. Bauer; New J. Phys. 7, (2005) 68

We used photoemission electron microscopy (PEEM) to investigate the lateral distribution of the photoemission yield from a defined system of silver clusters supported by a highly oriented pyrolytic graphite (HOPG) substrate. For threshold photoemission using conventional photoemission (PE) and twophoton photoemission (2PPE) we find that distinct, well-separated emitters are responsible for the measured integral photoemission yield. Complementary characterization of the surface usingSTMshows that the emitter density as probed by PEEM is reduced by about three orders of magnitude in comparison to the actual cluster density. Wavelength and light polarization scans in combination with two-photon-PEEM clearly show that the origin of the 2PPE signal is related to small silver particles. Furthermore, the PEEM differentiates between inhomogeneous and homogeneous broadening effects in the 2PPE signal. This observation allows one to assign the origin of the local photoemission signal to either a distinct single silver particle or a number of coherently coupled silver particles. We conclude that the 2PPE-yield is highly selective with respect to specific properties of the supported silver particles. Our results show that in future experiments, PEEM as a highly local field probe, may be a key tool in the identification of these properties.

Spin Dynamics of GaAs(100) by Two Photon Photoemission
L. Guo, J. P. Wüstenberg, O. Andreyev, M. Bauer, M. Aeschlimann; Acta Physica Sinica Vol. 54 No. 7 (2005)

Femtosecond ultraviolet photoemission for the study of ultrafast surface processes (topical review)
M. Bauer; J. Phys. D: Appl. Phys. 38 (2005) R253-R267

Conventional ultraviolet photoelectron spectroscopy (UPS) has been successfully used for decades to study static electronic properties of surfaces and their interaction with adsorbates. The recent progress in the creation of femtosecond and attosecond VUV pulses by means of high-order harmonic generation opens the potential to operate UPS in a time-resolved mode, which is capable of monitoring ultra-fast dynamical changes of surface properties. Particularly, it is now possible to evaluate the temporal evolution of chemical surface reactions on their fundamental time scales. This paper reviews technical aspects of time-resolved UPS and its application to the study of ultra-fast surface processes. Special emphasis is placed on the creation of ultra-short VUVpulses by means of high-order harmonic generation and also on the description of the stroboscopic experimental approach that enables temporal resolutions on the order of femtoseconds. This review will show that time-resolved UPS is indeed capable of probing with femtosecond resolution dynamic surface processes related, for example, to electronic excitations at surfaces or to the chemical state of adsorbates on a femtosecond time scale.

Time-resolved 2PPE: Probing adsorbate motion on femtosecond time-scales - what is the role of the laser bandwidth?
M. Bauer, M. Wessendorf, D. Hoffmann, C. Wiemann, A. Mönnich, M. Aeschlimann; Appl. Phys. A 80, (2005) 987

Recently it has been shown that time-resolved two photon photoemission spectroscopy (TR 2PPE) is capable of probing the atomic motion of an adsorbate after excitation by a femtosecond laser-pulse. In this paper we address the question in how far the bandwidth of the used laser pulse is of importance with respect to the sensitivity of TR 2PPE to the actual nuclear dynamics. In particular, we find that the use of laser pulses of different spectral bandwidth may simplify the interpretation of the measured TR 2PPE autocorrelation traces and help to distinguish between purely electron related contributions and the nuclear dynamics. Our experimental results indicate that for pulses of small bandwidth only the lifetime of the electronic adsorbate excitation at the ground state equilibrium distance is probed. This information can be used as input for the interpretation of autocorrelation traces obtained with large bandwidth pulses, which in addition contain information about the nuclear dynamics of the adsorbate.

Irridation of supported silver and gold nanoparticles with continuous-wave, nanosecond and femtosecond laser light: a comparative study

F. Hubenthal, M. Aschinger, M. Bauer, D. Blazquez Sanchez, N. Borg, M. Brezeanu, R. Frese, C. Hendrich, B. Krohn, M. Aeschlimann, F. Träger; Proc. of the SPIE 5838 (2005) 224

Modification of metal nanoparticles with laser light has been a well-known technique for several years. Still, selective tailoring of certain sizes or shapes of nanoparticles has remained a challenge. In this paper, we present recent studies on tailoring the size and shape of supported nanoparticles with continuous-wave and femtosecond pulsed laser light and compare them to our results obtained with ns pulsed laser light. The underlying method is based on the size and shape dependent plasmon resonance frequencies of the nanoparticles. In principle, irradiation with a given laser photon energy excites and heats nanoparticles of certain sizes or/and shapes and leads to difusion and evaporation of surface atoms. Thus, tailoring the dimensions of the nanoparticles can be accomplished. In our experiments, gold and silver nanoparticles were prepared under ultrahigh vacuum conditions by deposition of atoms and subsequent diffusion and nucleation, i.e. Volmer-Weber growth. This gives particle ensembles with size and shape distributions of approximately 30 % - 40 %. The nanoparticle ensembles were irradiated with laser light either during or after growth. It turns out, that irradiation with cw or ns laser light makes possible selective modifcation of the nanoparticles. In contrast, application of fs laser pulses results in non-selective modifcation. For example, post-grown irradiation of supported gold nanoparticles with ns laser pulses (hv = 1.9 eV) causes a clear reduction of the width of the surface plasmon resonance from 0.52 eV to 0.20 eV (HWHM). Similar experiments were carried out with fs pulsed laser light (hv = 1.55 eV), which result in a slightly reduced line width but also, to an overall decrease of the extinction. A comparison of all experiments revealed, that for size or shape tailoring of supported metal nanoparticles best results have been achieved with ns pulsed laser light.

2004

Lifetimes of excited electrons in Ta: experimental time-resolved photoemission data and first-principle GW+T theory
V. P. Zhukov, O. Andreyev, D. Hoffmann, M. Bauer, M. Aeschlimann, E. V. Chulkov, P. M. Echenique; Physical Review B 70, 233106 (2004)

Time-resolved two-photon photoemission spectroscopy and first-principles GW and GW+T theories have been used to study excited electron lifetimes in tantalum. The GW+T approach includes evaluation of the lowest self-energy term of the many-body perturbation theory in the GW approximation and higher terms in the T-matrix approximation. The GW+T calculated lifetimes are in good agreement with the measured lifetimes at excitation energies above 1.6 eV. At lower energies, a slightly worse agreement between theoretical and experimental data is obtained which we refer to as the influence of cascade processes.

Electronic Surface Structure of n-ML Ag/Cu(111) and Cs/n-ML Ag/Cu(111) as investigated by 2PPE and STS
M. Wessendorf, C. Wiemann, M. Bauer, M. Aeschlimann, M. A. Schneider, H. Brune, K. Kern; Appl. Phys. A 78, (2004) 183

We investigated the electronic structure of epitaxially grown silver films on Cu(111) with and without adsorption of cesium by means of scanning tunneling spectroscopy and two-photon photoemission. This system has been chosen as a model system to engineer and measure the dynamics of charge-transfer processes between an adsorbate and a heterogeneous substrate. Special emphasis has been laid on the investigation of the energy shift of the Shockley-type surface state and an excited cesium resonance as a function of Ag film thickness. For the cesium resonance we observe an increase in line width with increasing layer thickness.

2003

Hot-Electron-Driven Charge Transfer Processes on Surfaces
C. -F. Lei, M. Bauer, K. Read, R. Tobey, M. Murnane, H. Kapteyn; in Ultrafast Phenomena XIII: Proceedings of the 13th International Conference, (2003/2004) 313

We use ultrafast extreme-ultraviolet photoelectron spectroscopy to directly monitor the electron dynamics and the characteristic valence-band photoelectron spectra associated with a hot-electron mediated surface chemical reaction. By adsorbing molecular oxygen onto a Pt(111) surface and exciting it with an ultrafast laser pulse, charge transfer induced changes in the platinum-oxygen bond were observed on femtosecond time scales. By simultaneously monitoring both the hot-electron distribution at the Fermi edge and the valence-band photoemission spectra, it was determined that the thermalization of the hot-electron gas precedes significant changes in the O^2/Pt bond.

Time-resolved UPS: a new experimental technique for the study of surface chemical reactions on femtosecond timescales
M. Bauer, C. Lei, R. Tobey, M. M. Murnane, H. C. Kapteyn; Surf. Sci. 532 535, (2003), 1159

Recent progress in the generation of ultrashort XUV-pulses by means of high harmonic generation provides a means to monitor the dynamics of surface chemical reactions using photoemission spectroscopy. In this paper we describe details of an experimental setup for time-resolved photoemission spectroscopy using high harmonic generation. We als present results where the different steps involved in the laser-induced change of an adsorbate–surface bond were monitored with sub-100 femtosecond time-resolution.

2002

Imaging Sub-Nanosecond Processes Using Photoemission Electron Microscopy
G. Schönhense, A. Oelsner, A. Krasyuk, C. M. Schneider, M. Bauer, M. Aeschlimann; Recent Trends in Charged Particle Optics and Surface Physics Instrumentation, 8th Seminar, Brno (2002)

Dynamics of excited electrons in metals, thin films and nanostructures
M. Bauer, M. Aeschlimann; J. Electr. Spectr. 124, (2002) 225

The immense progress in the field of ultrashort pulsed lasers made it possible to study ultrafast dynamics of photoexcited hot electrons in metals by means of a variety of pump-probe techniques. Time-resolved two-photon photoemission has the capability of directly monitoring the dynamics of electrons with specific energy and momentum during the course of the transformation of a nascent (as photoexcited) nonthermal electron distribution to an excited Fermi–Dirac distribution. The main purpose of this investigation was to gain a basic understanding of the dynamics of single excited electrons at a metal surface, particularly in an energy region which is important for surface photochemistry and catalytic model reactions (E ,E,E). In these studies, the roles of secondary electrons and transport effects in equal pulse cross-correlation F Vac experiments were considered. The results demonstrate the feasibility of studying electron relaxation in noble and transition metals as a function of band structure, spin-polarization, surface morphology and dimensionality. We also present an extension of the common time-resolved two photon photoemission method to higher energies (hn.20 eV, UPS mode) and high lateral resolution (PEEM mode).

Time-resolved two photon photoemission electron microscopy
O. Schmidt, M. Bauer, C. Wiemann, R. Porath, M. Scharte, O. Andreyev, G. Schönhense, M. Aeschlimann; Appl. Phys. B 74, (2002) 223

Femtosecond, time-resolved two photon photoemission has been used to map the dynamics of photo-excited electrons at a structured metal/semiconductor surface. A photoemission microscope was employed as a spatially resolving electron detector. This novel setup has the potential to visualize variations of hot electron lifetimes in the femtosecond regime on heterogeneous sample surfaces and nanostructures.

Hot-electron-driven charge transfer processes on O2/Pt(111) surface probed by ultrafast extreme-ultraviolet pulses
C. Lei, M. Bauer, K. Read, R. Tobey, Y. Liu, T. Popmintchev, M. M. Murnane, H. C. Kapteyn; PRB 66 (2002) 245420
2001

We use ultrafast extreme-ultraviolet photoelectron spectroscopy to directly monitor the electron dynamics and the characteristic valence-band photoelectron spectra associated with a hot-electron mediated surface chemical reaction. By adsorbing molecular oxygen onto a Pt(111) surface and exciting it with an ultrafast laser pulse, charge transfer induced changes in the platinum-oxygen bond were observed on femtosecond time scales. By simultaneously monitoring both the hot-electron distribution at the Fermi edge and the valence-band photoemission spectra, it was determined that the thermalization of the hot-electron gas precedes significant changes in the O2/Pt bond.

2001

Direct Observation of Surface Chemistry Using Ultrafast Soft-X-Ray Pulses
M. Bauer, C. Lei, K. Read, R. Tobey, J. Gland, M. M. Murnane, H. Kapteyn; Phys. Rev. Lett. 87, (2001) 025501; see also: "Shooting an X-ray movie", Phys. Rev. Focus, http://focus.aps.org/story/v8/st1*, 7 July 2001*

We present the first demonstration of the use of ultrafast extreme-ultraviolet pulses to directly monitor a surface chemical reaction on femtosecond time scales. By adsorbing molecular oxygen onto a platinum surface and exciting it with an ultrafast laser pulse, changes in the oxygen-platinum chemical bond on a subpicosecond time scale were observed through changes in the photoelectron spectra. This work demonstrates a powerful new technique for studying reactions of interest in catalysis and for probing changes of local order on surfaces on their fundamental time scale.

2000

Transport and dynamics of optically excited electrons in metals
M. Aeschlimann, M. Bauer, S. Pawlik, R. Knorren, G. Bouzerar, K. H. Bennemann; Appl. Phys. A 71 (2000)

Time-resolved two-photon photoemission, based on the equal-pulse correlation technique, is used to measure the energy relaxation and the transport of the photoexcited carriers in thin Ag and Au films. The energy-dependent relaxation time shows a significant thickness dependence in the Ag film, whereas for Au a much smaller effect is observed. These experimental observations are compared with a theoretical model based on the Boltzmann equation, which includes secondary (Auger) electrons and transport. A good agreement between experimental and theoretical results is found for Au. However, in our calculations, we did not find any significant change in the thickness dependence in the case of Ag. In order to explain the strong effect in Ag, we discuss the possibility of surface excitations.

1999

Snapshot of electronic surface excitation: Observing adsorbate dynamics with femtosecond time-resolution
M. Bauer, S. Pawlik, M. Aeschlimann; Proc. of the 10th Annual Symposium of the Center for Photoinduced Charge Transfer, Rochester (1999)

Decay dynamics of photoexcited alkali chemisorbates: Real-time investigations in the femtosecond regime
M. Bauer, S. Pawlik, M. Aeschlimann; Phys. Rev. B 60 (1999) 5016

The inelastic decay time of photoexcited cesium and sodium adsorbed on different single-crystal surfaces has been investigated by means of time-resolved two-photon photoemission. Especially in the case of cesium, we observe a surprisingly high lifetime. For Cs/Cu~111! we obtain a value of 15 fs. Intra-atomic hybridization, the specific band structure of the substrate, and adsorption site effects may be responsible for this behavior. These different mechanisms are discussed in detail.

1998

Electron dynamics of aluminum investigated by means of time-resolved photoemission
M. Bauer, S. Pawlik, M. Aeschlimann; Proc. of the SPIE, 3272 (1998) 201

Femtosecond time-resolved two photon photoemission has been used to investigate the dynamics of photoexcited electrons at a polycrystalline Al surface. The measured relaxation time data are very different from the behavior predicted for a Fermi Liquid. We observed a distinct increase in the decay rate of the excited states. The origin of this strong deviation from the theoretical prediction may be transport effects or band structure effects induced by the periodic crystal lattice.

Direct transition in the system Ag(111) studied by one and two photon photoemission
S. Pawlik, R. Burgermeister, M. Bauer, M. Aeschlimann; Surf. Sci., 402-404 (1998) 556

We report a Two-photon Photoemission study of an excited state of cesium adsorbed on a Cu(111) single crystal surface at submonolayer cesium coverage. The dependence of cesium excitation on the laser polarization enables us to make statements about the symmetry of the intermediate as well as the initial state of the 2PPE process.

Symmetry properties of an alkali excitation at a noble metal surface as investigated by two-photon photoemission
M. Bauer, S. Pawlik, R. Burgermeister, M. Aeschlimann; Surf. Sci., 402-404 (1998) 62

We report a Two-photon Photoemission study of an excited state of cesium adsorbed on a Cu(111) single crystal surface at submonolayer cesium coverage. The dependence of cesium excitation on the laser polarization enables us to make statements about the symmetry of the intermediate as well as the initial state of the 2PPE process.

Spin-dependent electron dynamics investigated by means of time- and spin-resolved photoemission
M. Aeschlimann, R. Burgermeister, S. Pawlik, M. Bauer, D. Oberli, W. Weber; J. Electr. Spectr., 88-91 (1998) 179

The power of time- and spin-resolved two photon photoemission is demonstrated. This method allows the determination of the spin-dependent decay of an excited electron population in ferromagnetic materials by means of a real time experiment. The lifetime of majority-spin electrons is found to be longer compared with that of minority-spin electrons for both cobalt and iron. This study shows that the relaxation dynamics of excited electrons is strongly influenced by the imbalance between majority- and minority-spin electrons in a ferromagnet.

1997

The resonance lifetime and energy of an excited Cs-state on Cu(111)
M. Bauer, S. Pawlik, M. Aeschlimann; Phys. Rev. B. 55 (1997) 10040

Using time-resolved two-photon photoemission spectroscopy, we investigated the resonance lifetime and energy of an excited Cs-state on Cu(111) in the low-coverage case. We found a pronounced lifetime increase of up to 11 3fs on a copper surface covered with cesium as compared to a clean copper surface in the energy range of an excited electronic Cs-state in the spectrum. This result is in agreement with recent theoretical predictions of hybridization among excited atomic levels of alkali atoms near metal surfaces.

Ultrafast spin-dependent electron dynamics in fcc Co
M. Aeschlimann, M. Bauer, S. Pawlik, W. Weber, R. Burgermeister, D. Oberli, H. C. Siegmann; Phys. Rev. Lett. 79 (1997) 5158

The unambigious observation of a spin dependent lifetime in a 200 A-thick fcc Co film on Cu(100) substrate by means of a femtosecond realtime experiment is reported. Using time- and spin resolved two photon photoemission technique, a ration of majority- to minority-spin lifetimes of 1.4 is obtained at low energies. The results demonstrate the feasibility of studying spin-dependent electron relaxation in ferromagnetic solids directly in the time domain and provide a framework for understanding the dynamics of electron transport in ferromagnetic solids and thin films.

Femtosecond lifetime investigations of hot electrons trapped by adsorbate states: Atomic Oxygen on Cu(111)
M. Bauer, S. Pawlik, M. Aeschlimann; Surf. Sci. 377-379 (1997) 350

We investigated an excited electronic state induced by atomic oxygen adsorbed on Cu(111) by means of time-resolved two-photon photoemission spectroscopy. In contrast to a system investigated previously, cesium adsorbed on Cu(ill), no increase in the relaxation time of the photoexcited electrons due to the resonance time of the excited oxygen state was detected within our time resolution. The difference between the two systems will be discussed, taking the specific adsorption sites of the adsorbates on the Cu(111) surface into consideration.

Lifetime difference of photoexcited electrons between intraband and interband transitions
S. Pawlik, M. Bauer, M. Aeschlimann; Surf. Sci. 377-379 (1997) 206

Using time-resolved two-photon photoemission, we show that the inelastic lifetime r,, of optically excited electrons of copper depends crucially on whether the electron is excited by an intraband or an interband transition. These results indicate clearly that z,, of photoexcited electrons is determined not only by the available phase space for the inelastic scattering process, but also depends on the initial state of the excited electron.

1996

Dynamics of photoinduced surface reactions
S. Pawlik, M. Bauer, M. Aeschlimann; in "Femtochemistry: Ultrafast Chemical and Physical Processes in Molecular Systems", Edited by: M. Chergui, World Scientific Publishing (1996)

Competing nonradiative channels for hot electron induced surface photochemistry
M. Aeschlimann, M. Bauer, S. Pawlik; Chem. Phys., 205 (1996) 127

We report experiments in which we investigated the ultrafast dynamics of competing nonradiative channels for hot electron mechanisms in various polycrystalline metal samples. Time resolved two-photon photoemission, based on the equal pulse correlation technique, is used to measure the energy relaxation and the transport of the photoexcited carriers. In these studies the role of coherent effects in auto- and crosscorrelation experiments has been considered. While the inelastic lifetime of Ag is in qualitative and quantitative agreement with the Fermi liquid theory, the result obtained for Au is very different. The measured inelastic relaxation time for transition metals with unoccupied d orbitals is shorter as compared to the noble metals. The results demonstrate the feasibility of studying electron relaxation in noble and transition metals directly in the time domain and provide a framework for understanding the dynamics of hot electron transfer from a metal surface to the adsorbate.

1995

Femtosecond Time-Resolved Measurement of Electron Relaxation at Metal Surfaces
M. Aeschlimann, M. Bauer, S. Pawlik; Ber. Bunsenges. Phys. Chem. 99 (1995) 1504

Time resolved two-photon photoemission, based on the equal pulse correlation technique, is used to measure the energy relaxation of the photoexcited electrons in various polycrystalline metal samples. While for Ag the inelastic lifetime of excited electrons is, within our time resolution, in agreement with the Fermi-liquid theory, the result obtained for Au is very different. Scanning tunneling microscopy studies reveal that the enhanced inelastic lifetime of gold is not caused by surface effects. The measured inelastic relaxation time for transition metals with unoccupied d-orbitals is shorter as compared to the noble metals, indicating that the inelastic decay depends on the number of unoccupied d-orbitals below the probed energy state.