Time-resolved X-ray Photoelectron Spectroscopy Techniques for the Study of Interfacial Charge Dynamics

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Abstract

X-ray photoelectron spectroscopy (XPS) is one of the most powerful techniques to quantitatively analyze the chemical composition and electronic structure of surfaces and interfaces in a non-destructive fashion. Extending this technique into the time domain has the exciting potential to shed new light on electronic and chemical dynamics at surfaces by revealing transient charge configurations with element- and site-specificity. Here, we describe prospects and challenges that are associated with the implementation of picosecond and femtosecond time-resolved X-ray photoelectron spectroscopy at third-generation synchrotrons and X-ray free-electron lasers, respectively. In particular, we discuss a series of laser-pump / X-ray-probe photoemission experiments performed on semiconductor surfaces, molecule-semiconductor interfaces, and films of semiconductor nanoparticles that demonstrate the high sensitivity of time-resolved XPS to light-induced charge carrier generation, diffusion and recombination within the space charge layers of these materials. Employing the showcase example of photo-induced electronic dynamics in a dye-sensitized semiconductor system, we highlight the unique possibility to probe heterogeneous charge transfer dynamics from both sides of an interface, i.e., from the perspective of the molecular electron donor and the semiconductor acceptor, simultaneously. Such capabilities will be crucial to improve our microscopic understanding of interfacial charge redistribution and associated chemical dynamics, which are at the heart of emerging energy conversion, solar fuel generation, and energy storage technologies.

Keywords: X-ray photoelectron spectroscopy; time-resolved; femtosecond; picosecond; free-electron laser; synchrotron radiation; ultrafast charge transfer; dye-sensitized; semiconductor interfaces; transient surface photo-voltage;

1. Introduction

Since the first demonstration of X-ray photoemission spectroscopy (XPS) by Siegbahn and co-workers in 1957 [1], the method has found widespread application in many areas of research and industry due to its capability to derive quantitative information on the atomic composition and electronic structure of solid and liquid surfaces. In particular, in the fields of surface physics and interfacial chemistry, it has been developed into a powerful spectroscopic tool that does not only reveal the presence of small traces of atomic species on a surface based on their characteristic electron binding energies, but also provides insight into their chemical environment. The latter manifests itself in so-called “chemical shifts” of the photoemission lines, which relate to the fact that the exact inner-shell binding energy of an atom sensitively depends on the available electronic charge that can screen a specific core-hole vacancy [2, 3].

Extending XPS into the time domain holds great promise to capture not only the final products of photophysical processes and chemical reactions, but would additionally allow access to the microscopic dynamics underlying, for example, (photo-) catalytic processes including short-lived intermediate states. The history of time-dependent XPS studies traces back approximately twenty five years [4, 5] and may, traditionally, be divided into two broad categories, which either use fast data acquisition or pump/probe techniques. Enabled by the high X-ray brilliance available at third generation synchrotron light sources and the development of efficient electron energy analyzers and detectors, chemical reactions between molecules adsorbed from the gas phase onto metal surfaces have been followed on a few-second timescale

by fast sequential data acquisition [4, 6, 7]. However, this approach is generally restricted to the study of relatively slow reactions, since the time resolution in the experiments is limited by the minimum time needed to record an XPS spectrum with a sufficiently high signal-to-noise ratio [8]. By restricting the collection of fast XPS signals to a single binding energy, Hoefert et al. [9] recently demonstrated the possibility to follow adsorption and desorption kinetics of CO from Pt(111) with a temporal resolution of 500 μ s through averaging over hundreds of individual XPS time scans [9]. However, this approach requires precise prior knowledge of the evolution of the full XPS spectrum as function of process parameters, which may render the characterization of short-lived precursor states difficult.

Over the past ~15 years, time-resolved X-ray techniques have been introduced that make use of the pulsed time structure of X-rays emitted by synchrotron radiation facilities within a pump-probe scheme [10-19]. In this approach, a “pump” pulse initiates electronic and/or nuclear dynamics inside a target and their time evolution is monitored by a second, delayed X-ray “probe” pulse. In principle, the pump pulse can be any stimulus acting on the sample, such as a voltage [20], magnetic [21-23] or photon pulse [10, 13-15, 24, 25] as long as it is precisely synchronized to the probing X-rays. The time resolution within these experiments reaches the picosecond [11, 14, 15, 26-29] and even femtosecond [25, 30-32] regime.

We note that the vast majority of synchrotron-based time-resolved X-ray spectroscopy studies of photo-induced chemical and interfacial dynamics have, so far, not been based on XPS. Instead, the transient response of a sample to optical excitation has mostly been probed via the time-dependence of the X-ray fluorescence emitted from or X-ray intensity transmitted through the sample [11, 14, 15, 28, 29]. These time-resolved X-ray absorption spectroscopy (XAS) techniques have been successfully applied to uncover intra-molecular spin- and charge dynamics in isolated and solvated molecules [26, 27], and have recently been extended to probe charge transfer dynamics in dye-sensitized semiconductor nanoparticles [28, 29]. A time resolution of a few tens of picosecond, which is governed by the duration of the electron bunches in the storage ring, is routinely obtained in these experiments. A number of complementary time-domain X-ray techniques, such as femtosecond time-resolved XES [33-36] and high-field streaking experiments [37-39], have also been successfully applied by several groups to study ultrafast electronic and chemical dynamics in solid and liquid phase systems. We refer the reader to the

cited references and other contributions to this special issue for a more detailed discussion of these techniques.

Despite the distinct advantages offered by the high surface sensitivity of XPS compared to the more bulk-sensitive XAS techniques in the investigation of surface and interfacial chemistry, the development of time-resolved XPS at synchrotron facilities is still in an early stage. Up to now, it has been used almost exclusively to study the dynamics of transient surface photovoltage (SPV) phenomena at surfaces and interfaces of elemental semiconductors and metal oxides [5, 16, 19, 40-47]. First pioneering experiments have also addressed magnetization dynamics in thin films by taking advantage of the X-ray magnetic linear dichroism effect in photoemission [24]. However, one of the key capabilities of XPS - the detection of chemical shifts - has so far barely been exploited in the time-domain.

Generally, a transient charge redistributions around a probed atom is expected to induce a dynamical chemical shift of the corresponding core-level photoemission lines similar to time-dependent shifts of the absorption edges observed in time-resolved XAS experiments [29, 48]. In a recent pump-probe photoemission experiment performed with extreme ultraviolet (XUV) radiation produced by high-harmonic generation (HHG), the UV-induced electronic response in a self-assembled monolayer of iodophenylphenol on a Si(100) substrate could be followed on a few-picosecond timescale by selectively probing the inner-shell photoelectrons emitted from an iodine marker atom incorporated in the organic film [49]. Similar setups have been used to track the laser-induced bond-reconfiguration of oxygen atoms on a metal surface and the build-up of the SPV response in semiconductors with femtosecond resolution [50, 51]. Although these studies clearly demonstrate the prospects of time-resolved XPS to provide atomic-site specific real-time access to complex interfacial electron dynamics, HHG light sources still suffer from a limited energy range of the emitted radiation (≤ 200 eV [52]), which currently restricts their application to a relatively narrow range of inner-shell orbitals and model systems. HHG with significantly higher photon energies has been demonstrated, albeit with average intensities and/or pulse repetition rates that are, usually, too low for XPS applications [53]. New HHG techniques, however, are emerging rapidly and it appears to be only a matter of time until table-top femtosecond XPS setups will become available [54].

We note that HHG-based time-resolved photoemission spectroscopy (PES) on valence electrons is a fast expanding field of research. As opposed to XPS involving core-level

transitions, however, valence PES does, generally, not provide atomic site specificity, which is a central motivation for the work presented herein. Therefore, we refer the reader to the rich literature on time- (and angle-) resolved valence PES for an overview of its history and current trends (see e.g. [55-60] and references therein).

In this contribution, we discuss some possibilities offered by time-resolved XPS at third-generation synchrotrons and X-ray free-electron laser (FEL) facilities, which combine pico- and femtosecond temporal resolution, respectively, with a photon energy range covering the XUV, soft- and hard-X ray regions of the electromagnetic spectrum. Experimental implementations and associated challenges are described, in particular, for a picosecond time-resolved XPS apparatus recently commissioned at the Advanced Light Source (ALS) [12], and for a femtosecond time-resolved XPS experiment performed at the Linac Coherent Light Source (LCLS) [61]. Opportunities for sub-nanosecond time-resolved XPS using constant wave (CW) X-ray light sources will also be outlined [62]. Particular emphasis will be given to the ability of time-resolved XPS to follow charge carrier relaxation based on the transient SPV effect at semiconductor surfaces and buried interfaces. The light-induced electron injection and recombination dynamics at interfaces formed by N3 dye molecules (bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), see Fig. 7) adsorbed on films of ZnO nanoparticles are used to illustrate how dynamic chemical shifts in combination with SPV responses can provide comprehensive microscopic insight into transient electronic charge configurations in technologically pertinent hybrid systems.

2. Experimental Techniques and Instrumentation

X-ray FELs and synchrotron radiation facilities provide X-ray pulses that differ not only in their duration but also by orders of magnitude in repetition rates and pulse energies. The differences in pulse characteristics pose different challenges for the implementation of photoemission techniques at these facilities. In the following, we discuss strategies and schemes that have been adopted to take advantage of their characteristic beam properties in time-resolved XPS experiments.

2.1. High-repetition rate pump-probe XPS at synchrotron radiation facilities

The intrinsically pulsed nature of synchrotron radiation provides an opportunity for pump-probe studies with pulse repetition rates in the MHz range. The time resolution is, generally, limited by the duration of the electron bunches in the storage ring, which are typically in the range of 30-100 ps [14-16, 19] but may be reduced to few-ps [63, 64] or even sub-ps regimes [25, 65] using special (“low alpha”) storage ring operating modes and/or electron bunch slicing techniques.

A main challenge in synchrotron-based laser-pump/X-ray probe experiments often lies in the large mismatch in repetition rates of the optical pump lasers (kHz) and the synchrotron radiation (MHz). A common approach to address this issue is to synchronize the laser pulses with one specific electron bunch in the storage ring and to use gated detectors to suppress all X-ray signals except those associated with the selected bunch. Evidently, this scheme suffers from a significantly reduced data collection efficiency compared to static X-ray measurements, since only a small fraction of the available X-ray flux is used in the experiment. Beyond the cost of long data acquisition times, beam damage effects can become a decisive factor for the feasibility of experiments since a sample is still exposed to many X-ray pulses, but only a few contribute to the pump-probe signal. Therefore, an efficient implementation may require low-repetition fill patterns of the synchrotron, which, in turn, is often at odds with the demand for high brilliance X-ray radiation by the majority of the synchrotron user community. Nevertheless, this scheme provides the best time resolution, ultimately limited by the X-ray pulse length, which can even be pushed into the femtosecond regime [25]. In principle, fast detectors can be used to record and sort the data generated by all X-ray pulses in time [5, 9, 16, 17]. This time tagging method makes use of the full X-ray flux, and can even be used in combination with CW X-ray sources. However, the time resolution is usually in the nanosecond range and depends on the characteristics of the spectrometers, detectors and associated electronics.

The time-resolved XPS setup installed at beamline 11.0.2 of the ALS (Fig. 1(a)) combines the advantages of both detection principles. A hemispherical electron analyzer (HEA) (SPECS Phoibos 150 NAP) is equipped with a fast two-dimensional delay line detector (DLD) [66]. Photoelectrons are energy dispersed along one detector dimension while the second dimension encodes spatial or angular information depending on the lens mode of the analyzer. In addition to the detector hit positions, the arrival times of all photoelectrons reaching the detector are registered and processed by a time-to-digital converter (TDC). The analyzer is operated in

snapshot mode, which allows the recording of a fixed kinetic energy window (ca. 13% of the analyzer pass energy) without scanning the lens voltages.

Synchronization between the laser and the X-ray pulse train is achieved by an electronic scheme similar to those previously applied in time-resolved XAS experiments at the Advanced Photon Source (APS) and the Swiss Light Source (SLS) [14, 15] (Fig. 1(a), [12]): the ~500 MHz RF master clock of the ALS, which defines the electron bunch pattern in the storage ring and has a fixed phase relationship with the emitted X-ray pulse train, provides the primary reference signal. A fixed 1/6 frequency divider is used to scale the master clock signal frequency down to the ~83 MHz repetition rate of the laser oscillator. Using the phase-lock-loop of a commercial clock synchronizer unit (CLX-1100, Time Bandwidth Products), the oscillator frequency is stabilized to this reference with sub-ps precision by dynamically adjusting the cavity length with a piezo-actuated cavity end mirror. In a second branchline of the electronics, the 83 MHz oscillator reference signal is processed by a programmable frequency divider (PFD) and sent to a pulse picker that selects individual laser pulses from the phase-locked oscillator pulse train for further amplification at a user-defined repetition rate. The same signal is used as a start signal for the TDC to time-stamp the electron detector signals (see below). The laser/X-ray timing can be coarsely adjusted in steps of 12 ns (oscillator pulse spacing) by shifting the pulse-picker gate with a delay generator (DG). Fine-tuning of the pump-probe delay in steps of 5 ps over a range of 5 ns is achieved by using an electronic phase shifter in the oscillator reference signal line.

Fig. 1(b) shows a series of time-resolved XPS spectra in the range of the Au4f doublet obtained from a gold foil with a photon energy of $h\nu = 735$ eV and an electron analyzer pass energy of 150 eV. Fig. 1(c) shows the projection of the time-dependent XPS intensity at a kinetic energy (KE) of 650 eV in Fig. 1(b) onto the time axis, reproducing the ALS multi-bunch fill pattern. The particularly prominent, isolated spectrum in Fig. 1(b) is associated with the so-called camshaft bunch [67]. The capability of the setup to separate XPS spectra associated with different ALS pulses in multi-bunch operating mode generates new opportunities for efficient laser-pump multiple X-ray probe photoemission experiments that simultaneously capture dynamic processes on picosecond to microsecond timescales. We note that the overall accuracy for resolving the arrival times of photoelectrons is limited by their time-of-flight (TOF) spreads associated with different trajectories through the HEA lens system and hemisphere [62], which will be investigated in more detail in the following section. However, as long as the XPS signals

from individual synchrotron bunches can be separated in time, the timing accuracy of the synchronized laser-pump/X-ray-probe experiment is only limited by the X-ray pulse duration, since the arrival time of the X-rays is known with few-ps precision from the storage ring parameters.

A flexible high-power laser system (DUETTO, Time Bandwidth Products) is used to take full advantage of the high-repetition rate detection scheme. The system delivers 10 ps pulses with three selectable wavelengths (1064 nm, 532 nm and 355 nm) at adjustable repetition rates ranging from single shots up to 8 MHz. The laser output is commonly focused to beam diameters $\leq 200 \mu\text{m}$ (FWHM) commensurate with the typical X-ray spot sizes (Figs. 2(a) and (c)). This allows excitation fluences at the mJ/cm^2 level for laser repetition rates ≤ 1 MHz. The spatial overlap between the optical and the X-ray beams on the sample surface is tuned with a precision $\leq 20 \mu\text{m}$ (FWHM) by an iterative procedure of alternating knife-edge scans with the sharply defined edge of a photodiode, and adjusting the laser beam pointing with a piezo-actuated mirror mount (Fig. 2(c)). The long-term stability of the laser system's pulse energy and synchronization (Fig 2(b)) in combination with the highly stable synchrotron beam characteristics allows for extended periods of uninterrupted data acquisition time. These characteristics can significantly raise the detection limit in time-resolved XPS experiments. The flexibility of the setup is important for the capability to choose the optimum pump repetition rate suitable for a particular experiment, which depends on various parameters such as the relaxation/recovery time of the dynamic process of interest and laser-induced sample damage effects..

We note that previously described setups for synchrotron-based time-resolved XPS studies already implemented many aspects of the technique described herein, including, in particular, the use of time-stamping techniques [5, 16-19]. A very recent development is the integration of angle-resolved TOF spectrometers into time-resolved synchrotron photoemission experiments [18]. These setups combine a high transmission with full 2D angular detection, which makes them an interesting choice for band mapping and photoelectron diffraction applications. The key strengths of the setup presented here emerge from recent advances in both laser and detector technologies in combination with traditional strengths of HEAs. Commercial lasers now facilitate high repetition-rate pump-probe studies with high excitation fluences and operating stabilities commensurate with synchrotron light sources. Fast position-sensitive detectors in combination with HEAs offer simultaneous excellent time resolution and high-

efficiency data acquisition through fast snapshot modes that cover substantial electron KE windows with good energy resolution up to very high KEs and without the need for time-consuming energy scan procedures.

2.2 Prospects for Sub-Nanosecond Time-Resolved XPS with CW X-ray Sources

Many interesting interfacial phenomena such as charge carrier recombination and diffusion in hybrid molecular-semiconductor systems [68] and chemical kinetics in heterogeneous catalysis [69] exhibit dynamics in the nano-, micro-, or even millisecond range. Fast time-resolving detectors in combination with laboratory-based CW X-ray spectroscopy setups can provide an efficient means to probe these dynamics without the need to impose a time structure on the X-rays. To explore the limits of the achievable temporal resolution in such time tagging measurements, it is important to analyze the impact of the HEA on the overall time resolution.

The temporal resolution of a HEA is given by the TOF spread of the electrons that develops during their acceleration/deceleration inside the electrostatic lens system and while they are energy-dispersed within the hemisphere. Considering the hemisphere, there are two sources for this TOF spread: (i) Electrons with slightly different KEs, and therefore different velocities, can enter the hemisphere under slightly different angles and/or positions but arrive at the same position along the dispersive direction of the DLD. This effect is directly related to the HEA's finite energy resolution. (ii) The fundamental imaging properties of the hemisphere allow electrons with identical KEs to hit the DLD on the same energy-dispersed position after passing the hemisphere on trajectories with different path lengths. The most important analyzer parameters affecting both types of TOF spread are the pass energy, the sizes of the entrance and exit slits and the angular distribution of the electron trajectories at the hemisphere entrance slit [62].

By performing analytical calculations based on Kepler equations, as well as numerical simulations for the electron trajectories inside the hemisphere, we recently demonstrated that contribution (ii) by far dominates the overall TOF spread for the HEA used in the pump-probe XPS setup described in the previous section [62]. The analysis also revealed that the electrostatic lens system strongly impacts the final TOF spread by modifying the angular spread of the electrons at the entrance of the hemisphere depending on the ratio between the analyzer pass energy and the electron KE.

Experimentally, the evolution of the TOF spread as a function of KE can be characterized by recording XPS spectra induced by a pulsed X-ray source such as those shown in Fig. 1(b). An enlarged view of the section containing the camshaft-related signal is shown as a grayscale contour plot in Fig. 3(a). The centroids of the time histograms (cuts along the detection time axis) exhibit the intuitively expected trend that slower electrons arrive on the detector at later times compared to the faster ones. Fitting the individual time histograms to Gaussian profiles yields the TOF spreads summarized in Fig. 3(b). The FWHM time resolution is better than 3 ns across the entire (~ 16 eV wide) snapshot energy window. Furthermore, a TOF spread ≤ 500 ps is maintained between 649 eV and 653 eV – an energy range large enough to accommodate XPS lines including possible chemically shifted components. We note that these values are upper bounds for the HEA-induced TOF spreads, since the X-ray pulse duration (ca. 70 ps) and the DLD time resolution (180 ps) also contribute to the temporal response of the setup.

In agreement with previous studies, we find that the TOF spreads increase with decreasing pass energy. This trend is illustrated in Fig. 3(c), where the average TOF spread of a 7 eV wide KE window (643-650 eV) is plotted as a function of pass energy. Nevertheless, even for a rather small pass energy of 50 eV, a time resolution in the low nanosecond range is achieved. Since the energy resolution, the TOF spreads, and the size of the HEA snapshot energy window all depend sensitively on the pass energy, this parameter has to be individually chosen to meet the demands of a particular experiment. To our experience, a time resolution on the order of 20 ns (FWHM) or better is achieved for a very large range of pass energies and lens configurations, whereas a careful characterization of the HEA's temporal response as illustrated in Fig. 3 is mandatory to enable sub-ns resolution in time-resolved XPS solely based on the time tagging approach. Note that the details of the electron TOF/energy correlations are, generally, non-trivial, as illustrated by the complex structure of the grayscale map in Fig. 3a and the peak width dynamics in Fig. 3b. Some aspects of the electron trajectory induced TOF variations have been discussed by Shavorskiy et al. [62]. While a predictive understanding of all TOF/energy correlations is usually challenging, the general trends and, in particular, the achievable time resolution across a significant fraction of the XPS spectrum described above are good benchmarks for the overall functionality of the time tagging XPS technique.

2.3 Femtosecond time-resolved XPS

The time-resolved XPS schemes described in the previous sections can be used to track dynamics evolving on timescales of a few tens of picoseconds up to hundreds of microseconds. The desire to unravel even faster dynamics in complex systems with atomic site selectivity is an important motivation for the development of new light sources producing ultrashort X-ray pulses. Laser-slicing techniques have been successfully implemented at several synchrotrons to overcome the bunch-length limit for X-ray pulse durations [25]. Time-resolved experiments performed within this approach additionally benefit from an intrinsic pump-probe synchronization - provided the same laser system is used for the electron beam slicing and the experiment.

Even though this “femtosecond slicing” technique enabled several pioneering time-resolved XAS and X-ray diffraction experiments with a temporal resolution below 300 fs [30-32, 70], to the best of our knowledge no XPS experiments have been performed with such a source. A main challenge of the slicing technique is the significantly reduced number of photons per pulse since only a small fraction of a single storage ring electron bunch participates in the ultrashort X-ray pulse emission. Additionally, the pump-probe repetition rate is limited to a few kHz by the amplified femtosecond lasers needed to efficiently drive the slicing process. The resultant low X-ray flux entails long data acquisition times that are often incompatible with surface-sensitive photoemission spectroscopy, where sample contamination is a major concern even under ultra-high vacuum conditions.

Currently operational X-ray FELs can produce X-ray pulses shorter than 10 fs [71] and with extremely high peak powers but relatively low repetition rates (typically ≤ 120 Hz) [72]. Unfortunately, the high FEL pulse energies, which enable, e.g., single-shot X-ray diffractive imaging experiments, cannot be utilized in photoemission experiments. A large number of photoelectrons generated within a short time frame causes significant space charge effects. The electrostatic interaction between the photoelectrons on their way to the detector translates into substantial spectral distortions of their KE distributions [73]. Higher repetition rate FEL operating modes based on superconducting cavities are currently deployed or in preparation [74, 75] and will significantly improve the conditions for time-resolved XPS studies.

Pioneering ultrafast XPS studies performed at FLASH characterized the impact of femtosecond XUV induced space charge effects in FEL photoemission experiments on solids [73, 76], and were able to track the photo-induced loss of charge order in a Mott-insulator in real

time [77]. Pietzsch et al. analyzed the 4f photoemission from a W(110) surface at $h\nu = 119$ eV as a function of FEL pulse energy and found negligible space-charge induced spectral distortions for light intensities up to $\sim 10^8$ photons/pulse [76]. Studies of this kind provided first benchmark values for the optimum X-ray fluences for time-resolved FEL XPS experiments. However, the fluence threshold for space charge effects scales with the total electron emission yield of the sample material and, therefore, depends on a number of parameters, in particular, the photon energy and the sample composition. This implies that a careful characterization of the permissible X-ray fluence has to be performed as part of every FEL-based XPS experiment.

Building on the successful demonstration of femtosecond XPS with light sources below 150 eV photon energy, a time-resolved XPS study to capture ultrafast interfacial charge transfer dynamics in films of dye-sensitized nanocrystals has recently been performed at the LCLS using ~ 100 fs long X-ray pulses at 850 eV photon energy [61]. A schematic of the experiment at the LCLS Soft X-ray Materials Science (SXR) instrument is shown in Fig. 4. An optical (535 nm) pump laser is used to excite the dye molecules and initiate interfacial electron dynamics. Time-dependent photoemission spectra are recorded with a commercial HEA (Scienta R3000) on a shot-to-shot basis, enabled by triggering the readout of a fast CCD camera with a reference signal that is phase-locked to the 120 Hz repetition rate of the LCLS. The X-ray pulse intensity is reduced to $\sim 10^6$ photons/pulse using a combination of gas attenuators and metal absorbers to exclude distortion of the spectral features by space charge effects. The pump laser is operated at half the LCLS repetition rate to enable an interleaved acquisition of laser-on and laser-off (reference) XPS spectra, which minimizes the impact of long-term drifts in the experimental parameters on the XPS difference spectrum. The experiment is discussed in more detail in section 3.2.

3 Applications

In this section, we discuss selected experiments that demonstrate the potential of time-resolved XPS to monitor light-induced charge carrier dynamics at semiconductor surfaces and interfaces. In particular, the sensitivity of XPS to both the transient surface photo-voltage (SPV) response of the semiconductor material and the local valence charge density in the vicinity of specific atoms

is employed to view dynamics from both sides of molecule-semiconductor interfaces with exquisite site-specificity. By combining results from pico- and femtosecond time-resolved experiments on dye-sensitized ZnO nanoparticle films, we illustrate a concept for probing interfacial charge transfer dynamics via time-resolved XPS that is applicable to a broad range of molecule-semiconductor systems, which are at the heart of many emerging energy technologies.

3.1 Charge carrier recombination dynamics at semiconductor interfaces

The (photo)-catalytic activity of semiconductor surfaces and their performance in optoelectronic and photovoltaic applications is intimately linked to the photo-induced modulation of electron and hole densities at surfaces and interfaces [78, 79]. The widespread implications of the associated dynamic processes have recently motivated a series of pump-probe XPS studies that access the underlying charge carrier dynamics by monitoring the temporal evolution of the transient SPV initiated with pulsed infrared, visible, or UV laser excitation [5, 16, 40-47, 80, 81].

The sensitivity of XPS to a material's SPV response is schematically illustrated in Figs. 5(a), (b) using the example of a p-doped semiconductor. At the surface of a semiconductor, the position of the Fermi edge is essentially pinned near the middle of the bandgap by the large density of surface states (SS) [82]. Thermal equilibrium is achieved by charge exchange between the bulk and the surface ensuring a uniform Fermi level in the entire system. This charge redistribution gives rise to a space charge layer (SCL) that typically extends several tens of nanometers into the semiconductor [78, 82]. The electric field associated with the SCL induces a characteristic downward (upward) bending of all energy levels in a p-type (n-type) semiconductor toward the surface (Fig. 5(a)) [78, 82]. Under laser illumination with photon energies exceeding the semiconductor bandgap, electron-hole pairs are generated in the SCL, which partly screen this electric field, giving rise to a transient flattening of the energy bands near the surface (Fig. 5(b)) [78]. The timescale of this process depends on the diffusion and recombination dynamics of the electron-hole pairs. The SPV effect, therefore, manifests itself as a rigid, time-dependent shift of the entire XPS spectrum to lower (higher) effective binding energies for p-doped (n-doped) materials [5].

Fig. 5(c) shows an example of a pump-probe XPS experiment performed on p-doped GaAs(100) during two-bunch operation mode of the ALS using the apparatus described in section 2.1 [12]. The evolution of the effective Ga3d binding energy is plotted as a function of

the time delay between a 532 nm laser pump-pulse (~ 500 kHz; 10 nJ/cm^2) and a 450 eV X-ray probe pulse. The sudden shift of the Ga3d line position toward lower binding energies signals the build-up of the laser-induced SPV at the surface. It is followed by a much slower relaxation of the SPV on a nanosecond timescale. The observed binding energy variations due to a transient SPV are not to be confused with chemical shifts, which are induced by charge-rearrangements on (sub-)molecular length scales. In contrast, the SPV effect relies on a delocalized, electronic polarization response within the SCL.

The maximum SPV shift fully develops within ~ 70 ps (lower inset in Fig. 5(c)), which matches the previously reported X-ray pulse duration of the ALS [19]. This observation agrees with an intrinsic rise time of < 1 ps for the SPV response in GaAs as determined in a HHG-based photoemission study [51], which effectively limits the response time at the ALS to the X-ray pulse duration. The SPV decay is clearly resolved and involves at least two dynamic timescales: a fast component quenching the overall SPV by almost 40% within the first ~ 200 ps after excitation, and a second recombination process which is associated with a distinctly slower decrease over several nanoseconds. Indeed, the dynamics are well described using a bi-exponential decay model with time constants of 80 ± 30 ps and 2.3 ± 0.4 ns (red line in Fig 5(c)). However, the ~ -50 meV offset in Fig. 5(c) indicates that the SPV has not fully decayed within the period between two consecutive laser pulses ($2 \mu\text{s}$). An additional recombination channel with a time constant in the microsecond range is, therefore, also expected to contribute to the overall SPV relaxation.

SPV decay dynamics have been studied for a broad range of systems including clean surfaces of elemental [42, 43] and binary semiconductors [44, 83], as well as metal-oxides [43, 45, 80] and adsorbate-covered surfaces [44, 46]. The timescales of the SPV relaxation were found to be affected by surface preparation and orientation [5, 45, 80], doping [84], temperature [83], and the presence of adsorbates [44, 46, 83]. We note that the experiments on GaAs and ZnO/Si (see below) reported here have not been performed under ultra-high vacuum conditions, and no in situ sample cleaning has been applied. The exact dynamic time scales described here, therefore, differ from those reported for atomically clean surfaces. The qualitative trends in the SPV dynamics, however, are similar and illustrate the wealth of information that is encoded in the transient XPS spectra.

Biphasic SPV decay behavior, as highlighted in Fig. 5(c), has been observed for a large variety of systems [42, 43, 46, 47, 80, 84], which points to a generic involvement of two or more contributions to the fundamental relaxation mechanisms in photo-excited semiconductors. Unfortunately, to the best of our knowledge, no generally applicable description of SPV dynamics based on first principles is currently available. However, empirical models have been suggested, which usually include one or more phenomenological parameters that are adjusted in the attempt to describe measured transient SPV curves by the model functions. A deep understanding of the underlying physics, however, remains challenging.

The recombination of photo-induced electron hole pairs is governed by the probability that the bulk majority charge carriers - for which the band-bending represents a potential barrier - reach the minority carriers trapped at the surface. In Fig. 5(b) this corresponds to the migration of photo-generated holes from the bulk to the surface. In principle, this charge transfer to the surface can proceed via quantum-mechanical tunneling through the surface potential barrier or by thermionic emission [40, 42, 43, 46]. In the interpretation of recent SPV experiments, the latter has been proposed to generally lead to slower recombination dynamics than the tunneling mechanism [42, 46, 85].

Within the thermionic emission model, the effective barrier height itself increases as the original band bending recovers during the SPV relaxation, leading to a gradual reduction of the recombination efficiency. These decelerated SPV decay dynamics can be expressed as [40]:

$$SPV(t) = -\alpha kT \ln \left(1 - (1 - e^{-\frac{SPV_0}{\alpha kT}}) e^{-t/\tau_d} \right), \quad (1)$$

with SPV_0 being the maximum SPV shift, τ_d the dark carrier lifetime (i.e. the lifetime in the absence of any SPV) and α a dimensionless phenomenological parameter. The latter has been interpreted as a transmission probability similar to the ideality factor used in the theoretical description of Schottky diodes [40]. Neglecting a possible tunneling contribution, Eq. 1 has been successfully used to describe the full SPV dynamics for Si(111) [43], SiO₂/Si(100) [40], ZnO [43, 45] and TiO₂ [46], with α varying between 0.5 and 2. Moreover, rather different values for α and τ_d have been suggested for different ZnO surface orientations [43, 45]. Interestingly, the dynamics in Fig. 5(c) cannot be described according to Eq. 1 but require two independent relaxation time scales, indicating that complex dynamics beyond the abovementioned model assumptions may already become apparent in relatively simple systems.

The delocalized nature of the electric fields originating from SCLs suggests that changes in the SPV may be reflected in XPS spectra even when the photoelectrons are released from regions outside the actual SCL [78]. This effect is demonstrated in Fig. 6(a), which summarizes the SPV dynamics observed for ca. 3 μm thick, sintered ZnO nanoparticle films deposited on p-doped Si(100). The same films also served as substrates for the dye-sensitized samples discussed in the following section [12]. Fig. 6(b) shows four of the traces from Fig. 6(a) normalized to the same maximum SPV response. The experiment was performed in the time-tagging only mode, i.e. without synchronization between the pump laser and the ALS (see section 2.2). In this case, the synchrotron effectively acts as a CW X-ray source, enabling the efficient measurement of transients spanning the entire ~ 10 μs time window of the experiment as defined by the ~ 100 kHz pump laser repetition rate.

The response of the system to 532 nm laser excitation is probed via the binding energies of Zn3d inner-shell photoelectrons ($h\nu = 850$ eV). The optical excitation density is varied over five orders of magnitude. For all laser fluences, we observe a steep decrease of the Zn3d binding energy upon arrival of the laser pulse with the subsequent relaxation lasting for several microseconds. The sign of this laser-induced energy shift suggests the transient SPV in the buried p-type silicon substrate is responsible for the observed dynamics, since ZnO is intrinsically n-doped [86] and its band gap of ~ 3.2 eV significantly exceeds the laser photon energy of 2.3 eV. The absence of any SPV response from the ZnO film is corroborated by experiments in which the film is deposited on a stainless steel substrate (black line in Fig. 6(a)). In this case, no laser-induced change in the Zn3d line position is observed for fluences up to $10 \text{ mJ}/\text{cm}^2$. Thus, although the ZnO film thickness significantly exceeds the electron escape depth [87], the SPV dynamics probed by the Zn3d photoemission are exclusively induced by the laser-excited electron-hole pairs in the SCL at the ZnO/Si boundary (Fig. 6(c)). This result clearly demonstrates the ability of time-resolved XPS to detect electronic dynamics at buried interfaces. A similar result has previously been reported for BaF₂/Si interfaces [41]. A conceptual understanding of this effect, which relies on the rigid relative alignment of the energy levels (band offsets) at the semiconductor-semiconductor interface, is illustrated in Figs. 6(d),(e).

A pronounced fluence dependence of the SPV recovery dynamics is evident from Figs. 6(a), (b). For laser fluences $> 17 \text{ } \mu\text{J}/\text{cm}^2$, the Zn3d line position does not relax back to the laser-off situation within the 10 μs pump laser period. The SPV associated with a steady-state

concentration of laser-excited electron-hole pairs inside the SCL is prominent as a constant binding energy offset for negative pump–probe delays in Fig. 6(a). Additionally, the relaxation time clearly increases with laser fluence up to $\sim 34 \mu\text{J}/\text{cm}^2$, whereas for higher fluences the timescale of the SPV decay seems to remain constant. We note that only for the lowest excitation density ($80 \text{ nJ}/\text{cm}^2$) the SPV dynamics can be reasonably well described within the thermionic emission model (red dashed line in Fig. 6(b)), indicating that the dynamics for larger fluences are not entirely captured by the model.

We recently observed very similar trends for the laser fluence dependence of the SPV relaxation in bare p-doped Si(100) substrates covered with their native oxide layer [62]. Generally, the SPV effect in the high-fluence regime is a largely unexplored field. Recently, Ogawa *et al.* reported an oscillatory relaxation behavior in Si(111) on a timescale of $\sim 100 \text{ ns}$ for excitation densities $> 1 \text{ mJ}/\text{cm}^2$, which has been interpreted as an indication for nonlinear effects in the charge carrier recombination dynamics [42, 88]. We do not observe any oscillations but a clear deviation from the thermionic emission model, which seems to describe the dynamics at lower fluences quite well.

We note that care has to be taken in the interpretation of absolute values for SPV shifts measured with time-resolved XPS. As pointed out by several authors, photoelectrons experience SPV-induced potential energy shifts not only in the moment of photoemission but also during their travel toward the analyzer [47, 89]. The exact magnitude of the measured shift is, therefore, governed by both the timescale on which the electrons reach the entrance of the detector and the timescale of the transient SPV [47, 89].

The large variety of experimental findings and the limited success in describing all SPV dynamics with relatively simple models emphasize that the microscopic details of the underlying dynamics are far from understood. The development of ab-initio based methods to model these fundamental process from first principles will be extremely helpful and, in combination with state-of-the-art time-resolved XPS experiments, could provide a substantially more advanced picture of photo-induced dynamics in semiconductor devices than available today.

3.2 Charge transfer dynamics in dye-sensitized films of semiconductor nanocrystals

Hybrid systems combining semiconductor nanostructures with adsorbed molecular sensitizers (dyes) have long been considered a promising route toward novel photovoltaic and

photocatalytic technologies. A predictive understanding, however, of the interfacial charge transfer dynamics between the two components has proven challenging. Overlapping spectroscopic signatures in the optical regime and the delocalized nature of valence excitations often lead to ambiguities in the interpretation of dynamic trends found in time-resolved experiments. The atomic site specificity of time-domain inner-shell spectroscopy has the potential to enable a new perspective on many of these dynamics. In the following we will use a time-resolved XPS study of interfacial electron dynamics in films of N3 dye-sensitized ZnO nanoparticles to showcase the spatiotemporal sensitivity of the method.

The key idea of the approach is summarized in Figs. 7(a) and (b). A visible laser pump pulse promotes electrons from the highest occupied molecular orbital (HOMO) of the N3 molecule to its lowest unoccupied molecular orbital (LUMO), which is energetically aligned with the conduction band (CB) of the ZnO film. The temporal evolution of the excited-state electronic configuration is monitored by recording core-level photoelectron spectra of the N3 molecules as a function of the time delay between the laser excitation and the ionizing X-ray pulse. Charge exchange between the molecule and the substrate via electron injection and electron-hole recombination processes leads to characteristic fluctuations in the local charge densities around specific atoms, which translate into temporal variations of their inner-shell binding energies, i.e., transient chemical shifts. Probing these shifts for different core levels effectively provides an atomic site-specific view of the underlying electron dynamics.

The N3/ZnO system is particularly interesting since it has long defied high hopes to become a viable building block for dye-sensitized solar cells (DSSCs) but a comprehensive microscopic picture of the competition between charge injection, trapping, and recombination that limits the interface performance has not yet emerged. Light absorption in N3 proceeds via excitation of a singlet metal-to-ligand charge transfer ¹MLCT state. In principle, the subsequent depopulation of this initially excited state may proceed via direct (<100 fs) electron injection into the substrate CB or via intramolecular relaxation to the metastable ³MLCT triplet state, followed by much slower electron injection (10–100 ps). The relative importance of both channels may depend on the coupling strength for a specific dye–semiconductor combination.

A number of studies revealed that for N3/ZnO – in contrast to N3/TiO₂ – the generation of free charge carriers inside the semiconductor is delayed by several tens of picoseconds with respect to the optical excitation, which is consistent with the general observation of a lower

performance of ZnO-based DSSCs [90, 91]. The question remained, however, as to where the initially excited electrons are located (i.e. “stuck”) until their final release into the CB: on the dye in its $^3\text{MLCT}$ state or temporally trapped at the molecule/substrate interface. As schematically shown in Fig. 7(c), these two scenarios are marked by distinctly different spatial distributions of the excited electronic charge, which, in turn, corresponds to different expectation values for chemical shifts in the core shell energies of neighboring atoms.

For the time-resolved XPS experiment at the LCLS (Fig. 4), we concentrate on the C1s and Ru3d emission of the dye molecule, since this spectral region contains contribution from almost all atomic sites of N3 (Fig. 7(d)). C1s/Ru3d XPS spectra recorded with (red) and without (blue) 50 fs laser pulses (535 nm) preceding the probing X-ray pulses by (500 ± 140) fs are shown Fig. 8(a) [61]. The red spectrum in the upper panel of Fig. 8(a) exhibits a clear SPV induced, rigid shift to lower binding energies, which is associated with the Si support of the dye-sensitized film. After correcting for this effect, a difference remains between the spectra corresponding to a shift of a small fraction of the Ru3d doublet to higher binding energies (Fig. 8(a) middle and lower panels). Qualitatively, this observation can be rationalized by the fact that the MLCT leads to a reduced electron density near the metal center of the dye, which results in a less efficient screening of the Ru core holes. The exact magnitude of this dynamical chemical shift depends on the spatial separation of the HOMO hole-state (located predominantly at the metal center) and the excited valence electron density. For the scenarios shown in Fig. 7(c), constrained DFT calculations predict a Ru3d shift of ~ 0.8 eV for the $^3\text{MCLT}$ state configuration (I), ~ 3.4 eV for the completely ionized N3 molecule (III), and an intermediate shift of ~ 2.2 eV for a configuration in which the excited electron is confined to the interface (II) [61].

The lower panel in Fig. 8(a) shows the difference between the XPS spectra shown in the middle panel, i.e. after correction for the SPV-induced shift of the p-doped silicon substrate (section 3.1). The difference is marked by two characteristic maxima and minima, each separated by ~ 4 eV and closely resembles the simulated difference spectra of Fig. 7(c). Fitting the experimental data to a simulated difference spectrum - with the excitation yield and Ru3d chemical shift as the only free parameters - yields a transient chemical shift of 2.3 ± 0.2 eV. A similar shift was measured for a pump-probe delay of 1 ps. This strongly suggests the population of an intermediate electronic state located at the N3/ZnO interface that is formed within less than 500 fs and persists beyond the first picosecond after optical excitation (scenario (II) in Fig. 7(c)).

We note that an improper correction of the SPV-induced shift of the laser-excited spectrum yields a difference spectrum that is distinctively different from a transient Ru3d shift, which allows us to disentangle the intramolecular dynamics of N3 from the SPV response of the semiconductor substrate [61]. The lower panel in Fig. 7(d) illustrates the spectral fingerprint for different transient shifts of the Ru3d doublet (4.2 eV spin-orbit splitting) based on simulated XPS difference spectra assuming an optical excitation yield of 5%. The stark variation of the simulated difference spectra for three different chemical shifts of 1 eV, 2 eV, and 3 eV illustrates the sensitivity of the time-resolved XPS spectra to different local valence electron configurations and the reliability of the assignment that the measured transient chemical shift indicates an interfacial electron configuration rather than a molecular $^3\text{MLCT}$ state.

First results from picosecond time-resolved XPS measurements at the ALS that track the further temporal evolution of this interfacial charge transfer state are illustrated in Figs. 8(b) and (c), which show spectra obtained 30 ps and ~ 328 ns, respectively, after excitation with a 532 nm laser pulse [12]. Although the signal-to-noise in these particular measurements is not sufficient for a detailed analysis, a distinct difference spectrum is observed at a pump-probe delay of 30 ps that is compatible with a transient Ru3d shift on the order of 1.5-3 eV. In addition, the absence of such correlation for the difference spectrum shown in Fig. 8(c) indicates that after ~ 330 ns most of the laser-excited molecules have already been reduced back to their neutral ground state by electron back donation from the semiconductor CB into the N3 HOMO. Note that the more pronounced laser-induced change in the middle panel of Fig. 8(b) (ALS) compared to that of Fig. 8(a) (LCLS) does not necessarily reflect different physical effects. It is more likely the result of variations in the experimental conditions, which are challenging to control on this level of detail.

A closer inspection of the data presented in the upper panels of Figs. 8(a),(b) reveals that the SPV shift induced by the optical excitation are of opposite signs for different pump-probe delays: whereas the SPV effect 500 fs after laser excitation stems from the buried ZnO/p-Si interface (see previous section), the SPV observed on the picosecond timescale shows pronounced n-type behavior, i.e., a shift to higher binding energies. The complete temporal evolution of this shift is summarized in Fig. 9(a) [12]. It was recorded with a laser-pump/multiple X-ray probe experimental scheme during ALS multi-bunch mode. The SPV rises to almost 500 meV within the time resolution of the experiment and rapidly decays to 40%

within only a few nanoseconds. The remaining SPV relaxes over several hundreds of nanoseconds.

We note that for the high laser fluences employed in the time-resolved XPS experiments ($\sim 10\text{-}15\text{ mJ/cm}^2$ for all spectra in Fig. 8), the SPV response of the ZnO/p-Si interface is essentially saturated on a μs timescale (see Fig. 6(a)), and can therefore not contribute to the nanosecond transient. This saturated SPV merely adds a constant, negative offset, which has been removed in Fig. 9(a). For comparison, the green crosses in Fig. 9(a) mark the results of the same pump-probe experiment on a bare, non-sensitized, sintered film of ZnO nanocrystals deposited on a stainless steel support. Despite the high laser fluence ($\sim 10\text{ mJ/cm}^2$), no trace of an SPV effect is observed in the bare film, reproducing the trend of the black trace in Fig. 6(a) and consistent with the fact that the photon energy of the 532 nm pump laser lies significantly below the $\sim 3.2\text{ eV}$ bandgap of ZnO.

Fig. 9(b) illustrates a microscopic explanation for the n-type nanosecond SPV response of the dye-sensitized film. Defects in the crystal structure of ZnO usually render it an n-type semiconductor [86]. Therefore, the sign of the transient SPV induced by direct electron-hole pair generation in ZnO is opposite to that in p-doped Si, i.e. effective electron binding energies tend to increase upon excitation. This has been demonstrated, for example, by SPV studies using super-bandgap ($>3.2\text{ eV}$) excitation of ZnO crystals with UV radiation [43, 45]. Here, we observe the same trend for the dye-sensitized ZnO film but not the bare substrate. We conclude that the SPV response in Fig. 9(a) does not stem from direct super-bandgap excitation of the ZnO substrate but from electron injection from the light-absorbing dye molecules into the semiconductor. The injected electrons diffuse into the SCL and screen the space charge, which leads to a lowering of the band bending near at the ZnO surface. The subsequent SPV decay is then governed by the interfacial recombination dynamics that refill the N3 HOMO hole-state. In the absence of additional electron donors (e.g. a dissolved redox species in the electrolyte of a working DSSC), this electronic charge has to be supplied by electron back-transfer from the SCL to the dye-cation, which restores the original band alignment.

We note that this picture is fully consistent with the p-type SPV observed 500 fs after photo-excitation, since electrons confined at the N3/ZnO interface cannot efficiently screen the positive space charge inside the semiconductor. The different SPV responses observed for pump-probe delays $\leq 1\text{ ps}$ and beyond $\sim 30\text{ ps}$ are, therefore, a confirmation of previous time-domain

studies, which indicate that injected electrons become available as mobile charge carriers in the semiconductor substrate on a tenth of nanosecond timescale [90-92]. We emphasize that the physical origins of all SPV effects discussed herein are associated with electronic dynamics within either the ZnO or the Si substrate, independent of the mechanism that induces these dynamics (super-bandgap excitation or electron injection). The adsorbed dye molecules are considered spatially separated and electronically isolated from one another. Therefore, they do not establish a bulk-like band structure, which would be a prerequisite to exhibit an SPV effect.

The SPV relaxation dynamics in N3/ZnO can be described using a bi-exponential decay model with time constants of ~ 10 ns and ~ 100 ns (red line in Fig. 9). However, the transient can be fitted equally well using the thermionic emission model (Eq.1) with a dark carrier lifetime $\tau_d = 390$ ns and $\alpha = 3$. While the timescales extracted from both fits fall well within the range of recombination times measured with optical transient absorption [93], the value for α is significantly larger than reported SPV dynamics in single crystalline ZnO samples after super-bandgap excitation [43, 45]. This discrepancy might be linked to the differences in the morphology of the ZnO samples (nanoporous vs. crystalline) and/or be an indication that different mechanisms are responsible for the SPV relaxation in bare semiconductor SCLs and at molecule-semiconductor interfaces [79]. This result further emphasizes the importance of a comprehensive theoretical description of space charge effects at hybrid semiconductor interfaces [94]. We note that even though the saturated SPV from the p-Si substrate does not directly contribute to the nanosecond SPV decay, it effectively acts as a DC bias applied across the N3/ZnO film, which might indirectly influence the overall charge separation and recombination process. Indeed, bias dependent recombination dynamics have been observed in DSCs [95], and represent an interesting target for future time-resolved XPS studies.

In addition, comparative time-resolved XPS studies of electron dynamics at N3/ZnO and N3/TiO₂ interfaces will be instructive, since electron injection in the latter system proceeds on a much faster time scale [96, 97]. This may either point to an ultra-short lifetime or the complete absence of interfacial charge transfer states for the N3/TiO₂ interface. In addition to XPS-based studies, complementary time-resolved XAS experiments at the absorption edges of the semiconductor substrate can provide further details on the spatial distribution of the electrons at the interface after injection, as recently demonstrated by Rittman-Frank et al. for isolated TiO₂ nanoparticles [28].

Finally, we briefly comment on sample damage in time-resolved XPS experiments on dye-sensitized semiconductor materials. Managing sample damage induced by both the optical pump pulse and the probing X-rays is crucial for successful experiments. Extensive efforts have been spent to derive permissible fluences and exposure times including optical fluorescence microscopy and static XPS characterization [61]. While the relatively low 60 Hz optical / 120 Hz X-ray pulse repetition rates in the LCLS experiment enabled extended exposure times of ~15 min on a single sample spot with negligible damage, fast scanning of the sample position during the experiments is mandatory at the ALS due to the approximately three orders of magnitude higher pump-probe duty cycle. The effect of beam damage in the ALS experiments is illustrated in the inset of Fig. 9(a). The data were derived by scanning pump- and probe-beams over the same area of a nanoporous ZnO film sensitized with N3 dye molecules multiple times and recording the induced SPV effect. The scan speed was 120 $\mu\text{m/s}$, the laser fluence $\sim 10 \text{ mJ/cm}^2$. The graph shows the reduction of the SPV-shift relative to its original value at a fixed pump probe delay of 200 ps. While no damage effects are observed during the first two scans, the measured SPV drops rapidly for longer exposure times and reaches less than half of its original value during the 8th scan. In order to explore the optimal parameter range for the experiments, repetitive scans on the sample are performed with various excitation densities and scan speeds. Note that the decay of the SPV effect illustrated in the inset of Fig. 9(a) provides additional support for the conclusion that it is associated with electron injection from the dye molecules. Laser fluences on the order of $\sim 10 \text{ mJ/cm}^2$ are well below the damage threshold of the ZnO substrate [98]. Therefore, the decay of the SPV effect as a function of exposure time is likely associated with damage to the dye molecules and/or their attachment to the semiconductor, which, in turn, endorses the assignment of interfacial charge transfer as the origin of the SPV dynamics.

4 Conclusion and Outlook

Time-resolved XPS combines surface-, element-, and chemical sensitivity with high temporal resolution, which makes it uniquely suited for probing ultrafast interfacial electronic and chemical dynamics. Light-induced charge redistribution at semiconductor interfaces can be followed by tracking transient changes in the surface potential. Compared to more conventional Kelvin-probe spectroscopies, the higher temporal resolution offered by time-resolved XPS

enables access to charge carrier diffusion and recombination processes proceeding on picosecond and faster timescales. The simultaneous sensitivity of time-resolved XPS to the charge carrier dynamics inside a semiconductor substrate and the electronic configuration of adsorbed molecules provides a comprehensive, microscopic perspective of electronic charge flow across molecule-semiconductor hybrid interfaces from selectable atomic sites and from both sides of the interface. The next generation of free-electron laser facilities such as the European XFEL and LCLS-II are expected to significantly enhance the efficiency of femtosecond time-resolved XPS by compensating for space-charge limited X-ray pulse energies with orders of magnitude higher pulse repetition rates compared to existing X-ray FELs. This will enable comprehensive, highly differential studies of complex charge transfer and chemical dynamics from the viewpoints of different atoms within a hybrid interface configuration during a single FEL beam time.

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Figure Captions:

Fig.1. Picosecond time-resolved optical-pump/X-ray-probe XPS experiment at the Advanced Light Source (ALS). (a) Layout of the data acquisition and electronic synchronization scheme used to control the relative arrival times of the optical laser pump pulses and the X-ray probe pulses from the ALS. (DG = delay generator; TDC = time-to-digital converter). (b) 3D false-color representation of Au4f photoelectron spectra collected from a gold foil using a hemispherical electron energy analyzer equipped with a time- and position-sensitive delay-line detector (DLD). The photon energy was 735 eV and the analyzer was operated in snapshot mode with a detector TDC trigger derived from the ALS master clock. Each cut along the energy axis represents an XPS spectrum recorded at a well-defined time delay after this trigger, while a cut along the time axis at a fixed kinetic energy (shown as black line in the background) reflects the time structure of the X-ray pulse train. The total data acquisition time for all data in (b) was < 8 min. (c) The analyzer/detector combination can unambiguously separate spectra produced by individual X-ray pulses within the multi-bunch pattern of the ALS. (d) Fill pattern of the ALS during two- and multi-bunch operating mode and their relation to the timing in laser-pump/ multiple X-ray probe experiments.

Fig.2. Characteristics of the picosecond pump laser. (a) Pulse energy measured for different repetition rates. Inset: beam profile of the 532 nm output focused by an $f = 50$ cm lens. (b) Output power and locking noise of the phase-locked loop as a function of time. (c) Spatial profiles and overlap of the laser (red squares) and X-ray beam (black circles). Both beam profiles are obtained by scanning the edge of the photo-sensitive area of a diode (mounted on the sample holder) through the beams.

Fig.3. Characterization of the temporal resolution of the hemispherical electron analyzer. (a) Grayscale contour plot of Au4f photoelectron intensities generated by the camshaft X-ray pulse ($h\nu = 735$ eV) as a function of kinetic energy and arrival time at the detector. (b) Energy dependence of the full width at half maximum (FWHM) of the electron time-of-flight (TOF) spread. The FWHM and error bars are derived by Gaussian peak fits of the arrival time histograms. The inset shows a representative fit of the time histogram at a kinetic energy of 650 eV. (c) Impact of the pass energy on the average TOF spread within the 643-650 eV kinetic energy range.

Fig.4. Implementation of femtosecond time-resolved XPS at the Linac Coherent Light Source (LCLS). The optical pump laser is synchronized to the LCLS X-ray pulses and operated at half the LCLS repetition rate. The timing scheme enables an interleaved pump-on/pump-off data acquisition that minimizes the impact of long term drifts in both the X-ray and laser beam characteristics on the pump-probe XPS signal.

Fig.5. Charge carrier dynamics in p-GaAs(100) probed with picosecond time-resolved XPS. Illustration of the band bending at a p-type semiconductor surface and its impact on the measured XPS binding energies (a) without and (b) with laser illumination. See text for details. (c) Change of the effective Ga3d binding energy as function of time delay between a 532 nm laser pulse and the ionizing X-ray pulse ($h\nu = 450$ eV, data reproduced from Ref. [12]). The red solid line shows a fit to the data consisting of a bi-exponential decay convoluted with a Gaussian instrument response function (green line in lower inset). The upper inset compares a Ga3d XPS spectrum recorded in the absence (blue) and 200 ps after laser excitation (red). The Gaussian broadening of ~70 ps corresponds to the temporal resolution (FWHM) of the experiment, in this case the X-ray pulse length.

Fig.6. Charge carrier dynamics in buried semiconductor interfaces (data partly reproduced from Ref. [12]). (a) Change of the Zn3d binding energy as a function of pump-probe delay for different fluences of the 532 nm pump laser from a p-Si(001)/ZnO interface. The black line corresponds to data collected from a stainless steel/ZnO reference sample at the highest laser intensity, lacking any trace of the SPV dynamics that mark all Si/ZnO curves. (b) Same traces as in (a) but normalized to the same maximum change in the SPV shift to emphasize the fluence-dependent decay time scales. The black dashed line corresponds to a fit according to Eq. 1 with $\alpha = 1.4$ and $\tau_d = 2.4 \mu\text{s}$. None of the other curves can be described by Eq. 1, see text. (c) Schematic depiction of the experiment in real space. (d) and (e) The laser-induced change in band bending at the Si/ZnO interface indirectly affects the energy levels in the transparent ZnO film due to the fixed band discontinuity at the interface. The native interfacial silicon oxide layer and the upward band bending at the ZnO/vacuum interface are omitted for simplicity.

Fig.7. Concept for probing charge transfer at the N3/ZnO dye-semiconductor interface with time-resolved XPS. Illustration of the pump-probe principle in (a) real space and (b) energy domain (see text for details). (c) Schematic depiction of different charge configurations at the N3/ZnO interface: (I) metal-to-ligand-charge-transfer-state, (II) interfacial charge transfer state and (III) completely oxidized dye molecule. (d) Top: deconvolution of a stationary C1s/Ru3d XPS spectrum of N3. The inset indicates the atomic origin of the different components. In order of increasing binding energy, the lines correspond to the Ru3d_{5/2,3/2} doublet (purple), C1s from pyridine carbon atoms bound exclusively to other carbon atoms (blue), C1s from pyridine carbon atoms sharing bonds with nitrogen atoms (red), C1s from the isothiocyanate groups (turquoise), and C1s from the carboxylic acid groups (green). Middle: simulation of a laser-excited spectrum (red line) obtained by shifting 5% of the Ru3d component to $\Delta E = 2 \text{ eV}$ higher binding energy. The ground-state spectrum (blue line) is identical to the fit curve to the experimental spectrum (black line in upper panel). Bottom: simulated laser-on/laser-off difference spectra for different values of the chemical shift ΔE .

Fig.8. Femto- and picosecond time-resolved XPS on N3-sensitized, nanoporous ZnO [12, 61]. C1s/Ru3d XPS spectra measured at time delays of (a) $\Delta t = 500 \text{ fs}$ (LCLS), (b) $\Delta t = 30 \text{ ps}$ and (c) $\Delta t = 328 \text{ ns}$ (ALS) between a visible (532-535 nm) pump pulse and an 850 eV X-ray probe pulse are shown in the upper two rows. Top: raw data. Middle: SPV-corrected data. The insets highlight the laser-induced redistribution of spectral intensity in the range of the Ru3d_{5/2} line. Bottom: laser-on/laser-off difference spectra. A fit to the $\Delta t = 500 \text{ fs}$ difference spectrum (green line) reveals a $\Delta E = 2.3 \text{ eV}$ transient chemical shift of the Ru3d doublet to higher binding energies. The green shaded area in (b) indicates a range of difference spectra expected for chemical shifts between 1.5 eV and 3 eV.

Fig.9. Surface photo-voltage (SPV) dynamics at the N3/ZnO interface [12]. (a) SPV-induced shift of the C1s XPS spectrum as a function of pump-probe delay for N3/ZnO (blue crosses) and a bare ZnO film reference (green crosses). The red line corresponds to a bi-exponential decay model fitted to the data. Inset: characterization of sample damage by monitoring the evolution of the SPV shift at $\Delta t = 200 \text{ ps}$ for repetitive scans across the same sample region. (b) Schematic illustration of the interplay between electron injection and recombination dynamics at the N3/ZnO interface and the observed SPV response (see text for details).

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Figure_1

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SXR instrument at the LCLS

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Figure6