Femtosecond Time-Resolved Photoelectron Spectroscopy in the Extreme Ultraviolet Region

Dissertation

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Teile der Arbeit sind veröffentlicht in:

- **Laser-based apparatus for extended ultraviolet femtosecond time-resolved photoemission spectroscopy**

- **Application of monochromatized high harmonic EUV radiation for inner-shell photoelectron spectroscopy**
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Chapter 1

Introduction

The first article\textsuperscript{1} in the column “Research Highlights” of the Nature Physics Portal from 29\textsuperscript{th} November, 2001 was published under the synonym - “The Age of Attophysics”. The way to this scientific breakthrough\textsuperscript{2,3} is directly linked with the generation of light in the extreme ultraviolet (EUV) region proposed some ten years ago\textsuperscript{4}. Since then a rash progress\textsuperscript{5-7} has ended in the experimental evidence of a single attosecond pulse with a duration of 650±150 as. Considering that the attosecond pulse of such length is a coherent superposition of electromagnetic radiation with a bandwidth\textsuperscript{§} of 2.8 eV or 680 THz, which is likely the whole visible part of the electromagnetic spectrum, leads us to the conclusion that the carrier of such ultra-short pulses would be the EUV region. Consequently, in the following years we will be witnesses of the fast developing femto-and-attosecond time-resolved spectroscopy in the EUV region.

The development\textsuperscript{8} of short laser pulses and their applications for time-resolved measurements began in the early 70’s. The progress on laser pulse shortening is shown in Fig. 1.1. The first lasers working in the femtosecond region have been dye lasers. Practically all fascinating time-resolved measurements\textsuperscript{9-15} has been demonstrated in the 80’s. The fast changes of the transmittance and reflectivity of semiconductors, metals and liquids linked with inter- and intra-band transitions in semiconductors and metals, inter- and intra-molecular transitions in complex organic molecules, the rearrangement and breaking of chemical bonds

\textsuperscript{§} For chirp-free gaussian pulse the relation between the bandwidth $\Delta \nu$ and time duration $\Delta \tau$ is given as $\Delta \nu \cdot \Delta \tau = 0.441$
as well as the observation of phonons and excitons have been shown more than 10 years ago. Although the dye laser stability has been lower when compared to contemporary femtosecond lasers a pulse duration of less than 10 fs has been achieved with additional pulse spectral broadening via a self-phase modulation and subsequent pulse compression\textsuperscript{16,17}. In the early 90’s rapid development of femtosecond solid-state lasers resulted in the renaissance of the “old” time-resolved techniques and stimulated growth of new and more sophisticated measurements. Also the pulse duration\textsuperscript{18,19} of the femtosecond pulses in the visible has reached its limits of some 4.5 fs.

Parallel to these experiments in the visible, the nonlinear conversion of the visible light into the EUV, soft X-rays and hard X-rays regions stimulated by the development of TW femtosecond lasers\textsuperscript{21} has achieved great success and pushed the development of the theories (Fig. 1.2). The classical nonlinear optics\textsuperscript{22} based on the perturbation theory being a powerful tool of explaining $\chi^{(n)}$ processes has been not appliable to the new observed phenomena at intensities higher than 10\textsuperscript{14} W/cm\textsuperscript{2}. At these and higher intensities\textsuperscript{23} one is dealing with laser electric fields comparable to those in the atoms themselves and the electrons become ionized although the photon energies are much lower than the ionization potential of the atoms. Effects such as above-threshold ionization, high harmonic generation but also high energetic electrons\textsuperscript{24} and positrons\textsuperscript{25} generation has been observed and theoretically explained. Already

Fig. 1.1 Road map of the laser pulse duration (taken from Ref. 20 and updated)
at currently available intensities of some $10^{20}\ \text{W/cm}^2$ one can observe relativistic effects in the light-plasma interaction$^{26-30}$. 

### Regimes of Nonlinear Optics

<table>
<thead>
<tr>
<th>Perturbative regime</th>
<th>Strong-field regime</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bound electrons</strong></td>
<td><strong>Free electrons</strong></td>
</tr>
<tr>
<td>$\chi^{(2)}$ Processes</td>
<td>Multiphoton above-threshold ionization</td>
</tr>
<tr>
<td>Second harmonic generation</td>
<td>High harmonic generation</td>
</tr>
<tr>
<td>Optic parametric generation</td>
<td>Laser ablation</td>
</tr>
<tr>
<td>Optic rectification</td>
<td>Sub-fs x-ray and electron pulses</td>
</tr>
<tr>
<td>$\chi^{(3)}$ Processes</td>
<td>Long distance self-channeling</td>
</tr>
<tr>
<td>Third harmonic generation</td>
<td>Self-defocusing</td>
</tr>
<tr>
<td>Stimulated Raman scattering</td>
<td>Self-focusing and channeling</td>
</tr>
<tr>
<td>Self-phase modulation</td>
<td></td>
</tr>
<tr>
<td>Self-focusing</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1.2 Overview of the new regimes of nonlinear optics (taken from Ref. 23)

Another challenge that is closely connected with the generation of the light pulses with energies of few tens to few thousands of electronvolts is the measurement of their temporal duration and possible application for ultra-fast time-resolved techniques. The chart showing the progress on this field is compiled in Fig. 1.3. The pulse duration of the low-orders of high harmonics with energies up to 13.5 eV has been successfully measured with autocorrelation techniques based on two- and three-photon ionization$^{31-33}$. However, this method is not extendable to higher photon energies because of the extremely low transition probabilities of the non-resonant two and more photon ionization by the current high harmonics intensities.

Recently, high harmonics up to 40 eV photon energies have been characterized with cross-correlation techniques and utilised in time-resolved photoelectron spectroscopy measurements on adsorbates$^{34}$, isolators$^{35}$ and in the gas phase$^{36,37}$. Femtosecond pulse duration of high harmonics with a photon energy of 70 eV has been measured via hot electrons on a Pt surface in our Bielefelder-group described in chapter 5. Also stunning measurement of attosecond pulse duration of the high harmonics with an energy of 90 eV has been measured in the cooperation Vienna-Bielefeld$.^1$ The development of X-ray sources based on plasma recombination generated with high power femtosecond laser pulses on solid state
surfaces initiated the first hard X-ray time-resolved diffraction measurements. Recently, femtosecond pulse duration at photon energies of 4.5 keV\textsuperscript{38,39} and 8 keV\textsuperscript{40,41} were reported.

![Chart of demonstrated femtosecond or sub-femtosecond pulse duration with respect to their location in the electromagnetic spectrum.](image)

The aim of this thesis is to present two measurements that are contributing to the rapid growing field of femtosecond time-resolved spectroscopy in the EUV region. The first one demonstrates the selection of a single high harmonic without temporal distortion in a dedicated multilayer monochromator as proved by the measurement of its temporal duration with a cross-correlation technique based on hot electrons at the Pt surface. I have already shown a spectral selection\textsuperscript{35-47} of one high harmonic order. In chapter 5 I will report on the measurement\textsuperscript{48-50} of the 45\textsuperscript{th} high harmonic temporal duration. The peak photon flux of built high harmonic source compared to that of 3\textsuperscript{rd} generation storage ring\textsuperscript{51} (BESSY II) is shown in Fig. 1.4. The main advantage of high harmonic source as compared to such large scale facilities is the femtosecond time duration of high harmonic pulses. There are already first advances\textsuperscript{52,53} of a formation of synchrotron radiation with femtosecond pulse duration but until now no experiment has been demonstrated utilizing these pulses. The current drawback of the high harmonic sources is the low repetition rate of a few kHz compared to that of few hundred MHz of the storage rings\textsuperscript{51}. The second significant measurement presented in chapter 6 is the first application of a spectrally selected single high harmonic order for time-resolved core-level photoelectron spectroscopy. Recently published papers\textsuperscript{34-36} on time-resolved photoelectron spectroscopy using high harmonics are dealing exclusively with the valence bands or highest occupied molecular orbitals. Here I report on the first application\textsuperscript{54-57} for a femtosecond time-resolved study involving core-level electrons on the GaAs surface.
The extreme surface sensitivity of the photoemitted Ga-3d core-level electrons served for an observation of the charge transport and recombination after photoexcitation with the visible pump pulse.

Fig. 1.4 Performance of built high harmonic source compared to BESSY II (based on data from Ref. 51)
Chapter 2

Theoretical Background

2.1 Light–Solid Interaction

2.1.1 Photoexcitation and Photoemission

Under photoexcitation one understands the process when an electron after absorption of a photon will be excited into a binding state localized in the bulk or on the solid state surface. Photoemission stands for the process where the electron is excited into the continuum and escapes to vacuum. A simplified model of the metal and semiconductor electronic structure is shown in Fig. 2.1. The lowest photon energy needed for the photoemission is defined as the work function $\phi$ for the metals and $\chi + E_g$ for the semiconductors, where $\chi$ is the electron affinity and $E_g$ is the semiconductor band gap.

The probability of the photon absorption and electron transition from the initial state $|i\rangle$ to the final state $|f\rangle$ is given by

$$P_n = \frac{2\pi}{\hbar} \left| \langle f | H | i \rangle \right|^2 \delta(E_f - E_i - \hbar \omega)$$  \hspace{1cm} (2.1)

$^8$ The negative binding energies throughout this thesis are given relative to the Fermi level for the metals; relative to the top of the valence bands for semiconductors; and relative to the vacuum level for the rare gases.
Chapter 2 – Theoretical Background

Fig. 2.1 Scheme of the electronic structure of metal and semiconductor

$E_i$ and $E_f$ are the energies of the initial and the final electron states respectively and $H_i = e/mk \cdot A$, where $k$ is the electron momentum operator and $A$ is the vector potential. The energy conservation law is enforced with the delta function. In the case of the photoemission when the final state is not a bound state, the kinetic energy of the free electron is given by (2.2) and (2.3) for metals and semiconductors respectively

$$E_{kin} = \hbar \omega + E_i - \phi$$ (2.2)

$$E_{kin} = \hbar \omega + E_i - \chi - E_g$$ (2.3)

However, the probability of the photoexcitation and photoemission in the solid state is not given with the simple equation (2.1), but has to include the specific electronic structure of the examined specimen. After correction due to the variety of initial and final states and their dispersion with the electron momentum one can define the imaginary part of the dielectric function, which is proportional to the absorption coefficient by the photoexcitation and to the photoemission cross section in the case of photoemission respectively, as follows

$$\text{Im} (\varepsilon (\omega)) = \frac{1}{\varepsilon_0} \left( \frac{e}{m \omega \pi} \right)^2 \sum_{i,f} \int \left| \langle f(k) | H | i(k) \rangle \right|^2 \delta (E_f(k) - E_i(k) - \hbar \omega) d^3k$$ (2.4)
Fig. 2.2 Imaginary part of the dielectric function for Pt and GaAs (based on data from Ref. 62)

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.56</td>
</tr>
<tr>
<td>Al</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fig. 2.3 Electron inelastic mean free path for Al and GaAs (taken from Ref. 67, 68) and their lattice constants (taken from Ref. 61)
For illustration the imaginary parts of the dielectric function\textsuperscript{62} for two relevant solid states, Pt and GaAs, are shown in Fig. 2.2. Only the photons with an energy exceeding approx. 5.5 eV cause photoemission from the Pt and GaAs surfaces. Described as a three-step process\textsuperscript{65}, the photoemission consists of excitation, transport and escape of electrons from the solid state. During transport to the surface the final kinetic energy is reduced due to electron-electron (e-e) scattering and electron-phonon (e-p) scattering. As consequence of the inelastic scattering processes the collision mean free path of the electrons is drastically reduced as seen in Fig. 2.3. Electrons with a kinetic energy of about 50 eV typically possess an inelastic mean free path of less than 1 nm\textsuperscript{66-68}. Correspondingly, techniques probing electrons with kinetic energies around 50 eV are particularly surface sensitive, because 86\% of all electrons are originating from the first and second atomic layer of the solid state. A characteristic feature of the low kinetic energy electron spectra is a huge secondary electron background as result of the inelastic scattering processes.

\[
E_{\text{kin}} = m\hbar\omega - \phi
\]

![Fig. 2.4 Multiphoton photoemission processes](image)

As already noted, the photons with energies less than the work function for the metals or sum of the electron affinity and the band gap energy for the semiconductors can not promote electrons into vacuum. The situation changes when a huge amount of photons in a short time participate in the photoexcitation processes and nonlinear processes can be observed. Typical many-photon processes are summarized in Fig. 2.4. Let us speak about multiphoton emission\textsuperscript{69} (MPE) when an absorption of an appropriate number of photons stimulates the electron transition over the vacuum barrier. At even higher light intensities an electron that is already free due to MPE undertakes additional photon stimulated transitions in
continuum resulting in its final kinetic energy is $m\hbar\omega - \phi$, where $m$ is the number of the absorbed photons\textsuperscript{70} (see Fig. 2.4).

### 2.1.2 Relaxation Mechanisms in Metals

In general the relaxation mechanism describes the transition of the excited system back to the equilibrium. Such mechanisms are usually characterized with the energy and the phase relaxation times\textsuperscript{71-73}. 

![Diagram of a two level system coupled to the heat sink](image)

Fig. 2.5 Scheme of a two level system coupled to the heat sink

Suppose we have brought the simple two-niveau system (Fig. 2.5) in the excited state with the resonant light pulse. The relaxation induced via a dissipative system (heat sink) is described by the following equations in the density matrix formalism\textsuperscript{73}

\[ \frac{d}{dt} \rho_{10}(t) = -i \omega \rho_{10}(t) - \frac{1}{T_2} \rho_{10}(t) \quad (2.5) \]

\[ \frac{d}{dt} \rho_{11}(t) = -\frac{1}{T_1} (\rho_{11}(t) - \rho_{11}^{(eq)}) \quad (2.6) \]

\[ \rho_{01}(t) = \rho_{10}^{*}(t) \quad (2.7) \]

\[ \rho_{00}(t) = 1 - \rho_{11}(t) \quad (2.8) \]

where $\rho_{11}^{(eq)}$ denotes the thermal equilibrium and $T_1, T_2$ are the energy and the phase relaxation times, respectively. The elements of the density matrix $\rho_{ij}$ can be calculated as
\[ \rho_{ij} = \langle i | \hat{\rho} | j \rangle \quad i, j = 0, 1 \] \tag{2.9}

where \( \hat{\rho} \) is the density operator. The energy relaxation time \( T_1 \) characterizes the occupation decay \( \rho_{11}(t) \) of the upper level of the two-niveau system

\[ \rho_{11}(t) \sim \exp\left(-\frac{t}{T_1}\right) \] \tag{2.10}

The phase relaxation time \( T_2 \) describes the decay of the induced polarization \( P \) in the system with the excitation light pulse

\[ P \sim p_{10}\rho_{01} + p_{01}\rho_{10} \sim \exp\left(-\frac{t}{T_2}\right) \] \tag{2.11}

where \( p_{10} \) and \( p_{01} \) are the matrix elements of the atomic dipole operator. The energy relaxation time as well as the phase relaxation time are experimentally observable.

Most fundamental processes governing the excitation and relaxation processes in metals are summarized in Fig. 2.6. Dynamical screening describes the primary response of the valence electrons to the excitation light pulse. A macroscopic effect manifesting the dynamical
screening of electrons is the polarization of metals. Therefore all fundamental effects such as light reflection but also non-linear effects like second harmonic generation depending on the polarization of metals evolve on the attosecond time scale\textsuperscript{72,74}. Loss of the collective excitation coherence in the absence of the driving excitation light pulse is referred to as electronic decoherence\textsuperscript{72}. The phase relaxation time $T_2$ in the equations (2.5)-(2.8) is describing the loss of coherence in the observed system. Macroscopically, it can be observed as an exponential decay of the light-induced polarization of metals. In the last decade the interferometric time-resolved two-photon photoemission technique made direct observation of the electronic decoherence possible\textsuperscript{76}.

The reason for the electronic decoherence are mutual interactions of electrons such as the impurity and e-e scattering\textsuperscript{72,77}. In the case of electron scattering by charge impurity the electrons interact with charge impurities through the Coulomb potential\textsuperscript{77}. This process is elastic, that is the electron energy is conserved and only the direction of the electron momentum is changed. The electrons with lower kinetic energy are deflected more than electrons with higher kinetic energy by charged impurities. One of the most effective processes leading to decoherence is the e-e scattering\textsuperscript{72}. To clarify the e-e scattering let us use the concept of hot electrons, which are electrons excited above the Fermi level. A hot electron with momentum $k_1$ interacts with one electron below the Fermi level with the momentum $k_2$ through the Coulomb interaction to produce two hot electrons with energies less than the energy of the primary hot electron and momentum $k_1'$ and $k_2'$. The electron energies and momenta are given by

$$k_1 + k_2 = k_1' + k_2'$$  \hspace{1cm} (2.12)

$$E(k_1) + E(k_2) = E(k_1') + E(k_2')$$  \hspace{1cm} (2.13)

The characteristic e-e scattering time $\tau_{e-e}$ for hot electrons with the initial energy difference to the Fermi level $E - E_F$ derived by Fermi liquid theory (FLT) is\textsuperscript{72}

$$\tau_{e-e} = \tau_0 \left( \frac{E_F}{E - E_F} \right)^2$$  \hspace{1cm} (2.14)

where $\tau_0$ is given exclusively by the density of the electron gas\textsuperscript{72}. Direct measurement of the e-e scattering times / hot electron life times has been performed with the time-resolved two-
photon photoemission technique for series of noble and transition metals\textsuperscript{78-89} but also with traditional optical linear and non-linear time-resolved techniques\textsuperscript{94-97}. Typical measured hot electrons relaxation times\textsuperscript{89} for noble metals such as Ag and transition metals as Ni are shown in Fig. 2.7.

![Fig. 2.7 Measured hot electron relaxation times for Ag and Ni metals (taken from Ref. 89)](image)

A very important electron energy loss mechanism in the femtosecond and picosecond region is the e-p scattering\textsuperscript{71,72,77}. Populating the phonon modes in the e-p scattering leads to a rise of the lattice temperature. Typical energies of the phonons are a few tens of meV and therefore a lot of electron-phonon interactions are needed to lower the hot electron energy considerably. Phonons are acting as a heat sink for the thermalized hot electrons. The dynamics of the electrons and phonons is described by the following coupled differential equations in terms of the electron gas temperature $T_e$ and phonon gas (lattice) temperatures $T_l$\textsuperscript{98-100}

\begin{equation}
C_e \frac{\partial}{\partial t} T_e = \nabla_r (\kappa \cdot \nabla_r T_e) - g(T_e - T_l) + G(t)
\end{equation}

\begin{equation}
C_l \frac{\partial}{\partial t} T_l = g(T_e - T_l)
\end{equation}
where $C_e$ and $C_l$ are the heat capacities of the electrons and lattice, $G(t)$ is the optical generation term and $g$ is the electron-phonon coupling constant. The hot electron diffusion term with the electronic heat conductivity $\kappa$ is dominant in the first few picoseconds and therefore the term describing phonon diffusion has been neglected. To illustrate the “cooling” of hot electrons after initial pulsed photoexcitation of the platinum surface with an intensity of 32 GW/cm$^2$ the electron and lattice (phonon) temperatures are shown in Fig. 2.8. Rapid cooling of the thermalized hot electrons can be observed in the first few picoseconds.

![Fig. 2.8 Cooling of the electron gas via e-p scattering after photoexcitation with laser pulse on the Pt surface (taken from Ref. 100).](image)

All time-resolved techniques probing surface dynamics are measuring electron life times on surfaces, therefore surface-states$^{85,86}$ which are real states localized on the surface are playing a significant role in the hot electron relaxation. There is possibility of transfer of hot electrons to the surface-states and so to prolong electron life times. Also an electron transfer to empty states of adsorbates has been observed and measured$^{72,85,91-92}$. Auger processes leading to energy relaxation of hot-electrons in metals have been recognized as well$^{72}$.

A very important aspect of the electron relaxation in metals are transport effects$^{101,103}$. Almost every technique used to measure hot electron life times is surface sensitive, therefore electron transport into the bulk is affecting measured relaxation times$^{104}$. Summarized
electron relaxation processes together with the electron diffusion into the bulk are shown in Fig. 2.9. Pulsed photoexcitation promotes electrons into the unoccupied states above the Fermi level and produces a hot-electron population. At the same time the electrons are ejecting into the bulk and leaving the surface region with the velocity $\sim 1$ nm/fs (Fig. 2.9a).

In a short phase of few tens of femtoseconds after photoexcitation the hot electrons thermalize via e-e scattering and are characterized with the electron temperature $T_e$. During this time the lattice temperature $T_l$ is much smaller than the electron temperature $T_e$, while the surface region is depleting of electrons with the velocity of $10$ nm/ps (Fig. 2.9b). The third phase of the electron relaxation is characterized through the e-p scattering when “lattice heating” occurs due to thermalization of the electrons and phonons ($T_e \rightarrow T_l$). Typical electron transport velocities are about $100$ $\mu$m/µs which is conventional thermal diffusion.
2.1.3 Relaxation Mechanisms in Semiconductors

There are many similarities of relaxation processes in semiconductors with the processes in metals. The main differences have their origin in the band structure of the semiconductors and the correspondingly smaller density of free electrons. An overview of typical relaxation processes and their characteristic times is given in Fig. 2.10.

The coherent regime initiated with the photoexciting pulse is similar to the one in metals and is described with the coherence dephasing time (see eq. (2.11)).
Rapid loss of coherence has the same reason as in metals and is primarily connected with the fast e-e scattering\textsuperscript{71}. The e-e scattering is broadening the initial electron population distribution to the hot thermalized distribution (Fig. 2.10-1). At this stage the electron gas temperature is different from the phonon gas (lattice) temperature. The following phase is characterized through the e-p scattering\textsuperscript{108}. Phonon scattering processes are decreasing the electron gas temperature and increasing the lattice temperature. In semiconductors the e-p scattering is divided into two main groups – intervalley scattering and intravalley scattering. In intravalley scattering the electron - after interacting with phonon - stays in the same valence band valley (Fig. 2.10-2). The intervalley scattering transfers the electron to a different valley (Fig. 2.10-3). So electrons are scattering to the bottom of the conduction band where much slower processes occur, such as radiative recombination (Fig. 2.10-5), Auger recombination (Fig. 2.10-4), defect recombination (Fig. 2.10-6) in the bulk or the recombination via surface states. To illustrate the discussed processes Fig. 2.11 shows the time-resolved differential transmission measurement of a 0.5 $\mu$m GaAs film for $10^{17}$ cm$^{-3}$ excited carrier density\textsuperscript{107}. A fast decrease of the transmittance in the first few femtoseconds is attributed to e-e scattering whereas a slower decay is pointing to the e-p scattering.

Fig. 2.11 Time-resolved change of the GaAs transmittance for $10^{17}$ cm$^{-3}$ photoexcited carrier densities (adopted from Ref. 107)
Time-resolved studies based on two-photon photoemission has been applied to measure the electron dynamics on semiconductors surfaces as well\textsuperscript{109-111}.

The process of carrier diffusion is much more complex for semiconductors as compared to metals in the surface vicinity. The charge localized in the surface states (SS) is compensated via bulk electrons. For metals with a high density of electrons in the valence band this compensation is resulting in a dipole layer of only a few angstroms near the surface\textsuperscript{131}. Semiconductors with lower electron density in the valence band are building a space-charge region (SCR) which can extend few tens of nanometers into the bulk. Within the SCR the surface charge is compensated, leading to a band-bending in the surface vicinity\textsuperscript{132-138}. To shed more light on the phenomenon of band-bending let us suppose a n-type semiconductor with acceptor-type surface states. Electrons will be transferred to the empty surface states which results in a negative surface charge \(Q_{SS}\). To achieve equilibrium we need the same amount of positive space charge \(Q_{SC}\) under the surface to satisfy the net charge neutrality\textsuperscript{136}

\[
Q_{SC} + Q_{SS} = 0
\]  

(2.17)

As a result, the depleted zone of electrons – SCR will be formed. All potentials in the SCR have to fulfill Poisson’s equation\textsuperscript{136} for the new charge redistribution which results in an upward band-bending towards smaller effective binding energy. For p-type semiconductors with the donor type of surface states the situation will reverse whereby the surface charge \(Q_{SS}\) is positive and the space charge \(Q_{SC}\) is negative. In this case all bands bend downwards. In a first approximation the SCR width \(w\), the doping density \(N\) and the band-bending \(Y_0\) at the surface are coupled as follows\textsuperscript{136,139}

\[
w = \sqrt{\frac{2eY_0}{eN}}
\]  

(2.18)

where \(\varepsilon\) is the dielectric constant and \(e\) is the elementary charge. For example the p-GaAs with \(N = 10^{19}\) cm\(^{-3}\) and \(Y_0 = 0.7\) V has the SCR length of 10 nm. The potential change of 0.7 V over the range of 10 nm is responsible for very high electric fields of few hundreds of kV/cm in the SCR\textsuperscript{139}. Additional free electrons and holes injected by light absorption can change the band-bending. This phenomenon is called surface photovoltage (SPV) effect\textsuperscript{132-138}.
Chapter 2 – Theoretical Background

The dynamics of the photogenerated carriers - electrons and holes - neglecting the mentioned relaxation processes such as e-e and e-p scattering are described by the following coupled differential equations \(^{139-143}\)

\[
\frac{\partial n(z,t)}{\partial t} = G(z,t) + D_n \frac{\partial^2 n(z,t)}{\partial t^2} + \mu_n \frac{\partial}{\partial z} \left[ E(z,t) n(z,t) \right] - R_n \tag{2.19}
\]

\[
\frac{\partial p(z,t)}{\partial t} = G(z,t) + D_p \frac{\partial^2 p(z,t)}{\partial t^2} - \mu_p \frac{\partial}{\partial z} \left[ E(z,t) p(z,t) \right] - R_p \tag{2.20}
\]

\[
\frac{\partial^2 V(z,t)}{\partial z^2} = \frac{\partial E(z,t)}{\partial z} = \frac{e}{\varepsilon} \left[ p(z,t) - n(z,t) + N_d(z) - N_a(z) \right] \tag{2.21}
\]

The time-resolved band-bending \( Y = V(z=0,t) \) is given by the time-dependened densities of electrons \( n(z,t) \) and holes \( p(z,t) \) as well as by the densities of ionized donors \( N_d(z) \) and acceptors \( N_a(z) \). The dynamics of the electron density \( n(z,t) \) and hole density \( p(z,t) \) determine the continuity equation where \( G(z,t) \) is the optical generation term, \( D_n \) and \( D_p \) are the diffusion coefficients for electrons and holes, \( \mu_n \) and \( \mu_p \) are the electron and hole mobility. Recombination terms \( R_n \) and \( R_p \) are describing recombination processes \(^{143} \) such as radiative recombination \(^{139} \), defect – Shockley-Read-Hall recombination \(^{144} \) and Auger recombination \(^{143} \).
Surface recombination dynamics is given by two boundary conditions for electrons and holes\textsuperscript{143}

\[
\left. \frac{\partial n}{\partial z} \right|_{z=0} = \frac{(S_n + S'_n - \mu_e E(z = 0))}{D_e} n(z = 0, t)
\]
\hspace{1cm} (1.22)

\[
\left. \frac{\partial p}{\partial z} \right|_{z=0} = \frac{(S_p + S'_p - \mu_p E(z = 0))}{D_p} p(z = 0, t)
\]
\hspace{1cm} (1.23)

where $S_n$ and $S_p$ are the surface recombination velocities and $S'_n$ and $S'_p$ are the carrier transfer velocities characterizing processes like tunneling or thermionic emission. Equations (2.19)-(2.23) have no analytic solution\textsuperscript{143}. To illustrate the competing processes evolving after photoexcitation of a semiconductor surface let us suppose a p-type GaAs semiconductor surface (Fig. 2.12). Pulsed photoexcitation with a photon energy larger than the band gap produces electron-hole pairs. The presence of the high surface electric field separates the photogenerated electrons and holes, whereby the electrons move to the surface and the holes move further into the bulk. The change of the carrier density in the SCR flattens the original band-bending $Y_0$ to a new value $Y$. The electron mobility saturates\textsuperscript{139,140} for electric fields of some 100 kV/cm, for even higher fields the drift velocity therefore does not exceed 50 nm/ps. In this simple estimation the electron needs about 200 fs for transit through the SCR of 10 nm width\textsuperscript{145}.

\textbf{Fig. 2.13} Spatio-temporal evolution of the space charge field (taken from Ref. 169)
Fig. 2.14 Normalized time-resolved THz pulse wave and its spectrum (taken from Ref. 167)

The result of a detailed numerical study\textsuperscript{169} of the space charge field after delta-like pulsed photoexcitation of n-GaAs for the low carrier excitation density of $4 \times 10^{16}$ cm\textsuperscript{-3} and the low doping concentration of $10^{15}$ cm\textsuperscript{-3} is shown in Fig. 2.13. The decrease in the space charge field accompanied with an oscillatory behavior is pointing to a complex band-bending time evolution already at relatively small excitation intensities. Fast electron transfer in the SCR immediately after photoexcitation leads to radiative emission of the broad-band femtosecond far-infrared (FIR) THz pulses\textsuperscript{170-179}. The FIR field strength due to transient charge transfer is given directly as the second derivative of the space charge field\textsuperscript{167}. Measured FIR-THz pulse at different excitation densities of $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ cm\textsuperscript{-3} in p-GaAs (4x10\textsuperscript{14} cm\textsuperscript{-3}) together with their spectra are shown in Fig. 2.14. Femtosecond optically generated THz pulses in the SCR of semiconductors have found widespread application in THz time-resolved studies\textsuperscript{180-183}.

Once the electrons and holes have been separated and a new value of the band-bending has been achieved the relaxation processes take place. Besides the bulk recombination mechanisms like radiative, defect or Auger recombination, the surface offers new recombination possibilities like the surface recombination via surface states. The surface states act as recombination centers in the same manner as defect states\textsuperscript{144} in the bulk. Surface recombination\textsuperscript{146} can be relatively fast on the picosecond time scale\textsuperscript{147-153}. Direct measurements of the SPV dynamics on nanosecond and coarse picosecond time scales have already been published\textsuperscript{154-164}. These were based on an excitation laser synchronized with the probing soft x-ray storage ring pulses. In spite of these advances the fast SPV transients on the p-GaAs(100) surface have not been resolved as shown in Fig. 2.15. The SPV effect of the
anisotropic materials such as GaAs has been also measured with the pure optical
time-resolved methods\textsuperscript{142,166-168} making use of the electrooptic effect\textsuperscript{165} on the surface.

Fig. 2.15 SPV shift of the Ga-3d photoelectrons in p-GaAs at 125 K as a function of the delay
time between soft x-ray synchrotron pulse and excitation laser pulse (taken from Ref. 161)
2.2 Pump-Probe Technique

2.2.1 Principle of Pump-Probe Technique

One can observe ultrafast dynamics applying the so-called pump-probe techniques\(^{73,184}\). The general principle common to all types of pump-probe techniques is schematically shown in Fig. 2.16.

![Fig. 2.16 General scheme of pump-probe techniques](image)

The system initially in the equilibrium is optically excited into unoccupied states with the pump pulse. Once excited, the system relaxes back to the equilibrium states with the characteristic relaxation times (see section 2.1.2). A probe pulse with variable time-delay with respect to the pump pulse “maps” the changes in the relaxing system. Photons or electrons gated (=photoemitted, photodiffracted, up-converted etc.) by the probe pulse reflect the actual state of the system at the time of the probe pulse arrival. Scanning the time delay \(\tau\) between pump and probe pulses one can learn about the relaxation dynamics of the system.

Let us assume that relaxation of the system back to the equilibrium is described by the function \(f(t)\) after the excitation with the delta-like pump pulse \(\delta(t)\). The actual response of the system \(g(t)\) is described by the following convolution\(^{73,165}\) with the pump pulse’s temporal intensity profile \(h_{pu}(t)\).
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\[ g(t) = f(t) \times h_{pu}(t) = \int_{-\infty}^{\infty} f(\xi) \cdot h_{pu}(t - \xi) d\xi \]  \hspace{1cm} (2.24)

or Fourier transformed

\[ G(\omega) = F(\omega) H_{pu}(\omega) \]  \hspace{1cm} (2.25)

The measured signal \( m(t) \) gated by the time delayed probe pulse with the temporal intensity profile \( h_{pr}(t) \) can be written as convolution in the form

\[ m(t) = g(t) \times h_{pr}(t) = \int_{-\infty}^{\infty} g(\xi) \cdot h_{pr}(t - \xi) d\xi \]  \hspace{1cm} (2.26)

or Fourier-transformed

\[ M(\omega) = F(\omega) H_{pu}(\omega) H_{pr}(\omega) \]  \hspace{1cm} (2.27)

Now we can distinguish two limiting cases which simplify the derived equation (2.27). Let us assume that pump and probe intensity pulse profiles are delta-like functions. With this simplification the measured signal \( m(t) \) equals the function \( f(t) \). It means that we measure exclusively the relaxation of the investigated system without any influence of pumping and probing pulses. Another limiting case is when the relaxation function \( f(t) \) is a delta-like function. The measured signal \( m(t) \) now equals a cross-correlation of pump and probe pulses. This case gives an opportunity to measure the linear cross-correlation signal when the pump duration is considerably larger than the relaxation time of the system.

In pump-probe techniques one measures the photons or the electrons directly gated with the time delayed probe pulse under the assumption that the intensity of the probe pulse is smaller than that of the pump pulse. This means, that the influence of the probe pulse on the relaxation dynamics will be negligible. In practice, the following observables can be detected:

- absorption, transmission, reflection, diffraction, polarization of the “probe” photons
- nonlinear effects like second harmonic generation (SHG) of the “probe” photons
- fluorescence photons gated with the “probe” photons
- photocurrent due to photoexcited electrons by the “probe” photons
- photoelectrons emitted by the “probe” photons

Another difference between various pump-probe techniques is the propagation of pump and probe pulses. There are two principal possibilities of the mutual pump and probe propagation - collinear and non-collinear. Finally, time-resolved techniques can be phase sensitive or intensity sensitive. The phase sensitive time-resolved techniques are pushing the time-resolution under the duration of the pulse optical period cycle (400 nm = 1.33 fs)\(^{76}\).

A special class of the time-resolved techniques is the time-resolved photoelectron spectroscopy (TR-PES). This technique combines the classical photoelectron spectroscopy with the possibility to directly observe the transient changes of the electronic structure after photoexcitation. Photoexcitation of the valence electrons results in a transient population of normally unoccupied orbitals of molecules or bands of the solid state. The TR-PES techniques specializing on these transient electron populations utilize probe photons in the visible or ultraviolet region. A typical representative of this TR-PES class is the time-resolved two-photon photoemission (2PPE) technique\(^{72}\). Its principle is based on the following scheme for metals or semiconductors. The pump pulse excites the valence electrons into the unoccupied states above the Fermi level. After photoexcitation the probe pulse causes photoemission from the transiently occupied states. This technique provides one immediately with the relaxation times of the transiently occupied states. It has been developed for metals\(^{78-89}\), semiconductors\(^{109}\), clusters\(^{112}\) and molecules\(^{113}\). Exciting electrons into the unoccupied states can result in the photodissociation or photoisomerization of molecules, charge transport on the surfaces in semiconductors, desorption of adsorbates on metal surfaces and so forth. All mentioned processes can be detected as chemical shifts\(^{304}\) in the core-levels or changes in the valence band structures. Consequently, the probe photon energy must be in the vacuum ultraviolet (VUV) or EUV region for the valence band and core-level studies, respectively. The latter condition requires femtosecond pulses at least in the EUV region. Pioneering work in the field of EUV TR-PES was performed by Haight et al. who studied photoexcited semiconductor surfaces with few hundreds of femtoseconds resolution\(^{114-130}\). Recently, this techniques has also been applied to the adsorbate dynamics on a Pt surface\(^{34}\), the molecular dissociation of Br\(_2\)\(^{36,37}\), and hot-electron dynamics in quartz\(^{35}\).
2.2.2 Generation, Amplification and Application of Femtosecond Light Pulses

A light pulse of the femtosecond duration is a superposition of large number of the planar waves with different wavelengths but well defined phase conditions. Such pulse can be conveniently described in the following form\(^{73}\)

\[
E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(\omega) e^{i\phi(\omega)} e^{i\omega t} d\omega
\]  
(2.28)

where \(E(\omega)\) is the amplitude and \(\phi(\omega)\) is the phase of the complex spectral density \(\mathcal{E}(\omega) = E(\omega) e^{i\phi(\omega)}\). Generally the phase \(\phi(\omega)\) can be written as\(^{185}\)

\[
\phi(\omega) = \phi(\omega_0) + \phi'(\omega_0) \cdot (\omega - \omega_0) + \frac{1}{2} \phi''(\omega_0) \cdot (\omega - \omega_0)^2 + \frac{1}{6} \phi'''(\omega_0) \cdot (\omega - \omega_0)^3 + ... 
\]  
(2.29)

where \(\phi'(\omega_0)\) is called group velocity dispersion (GVD) term, \(\phi''(\omega_0)\) is called third order dispersion (TOD) term and so on. A pulse with a linear phase \(\phi(\omega)\) is a so-called Fourier-limited pulse and is the shortest achievable pulse for a given bandwidth \(E(\omega)\). The action of a linear optical system on femtosecond light pulses is given by the convolution of the impulse response function \(s(t)\) of the linear optical system\(^{73,75,165}\) and the femtosecond pulse \(E(t)\) and after Fourier transformation is simply given in the form

\[
\mathcal{E}_{\text{out}}(\omega) = S(\omega) e^{i\omega(\omega_0)} \mathcal{E}_{\text{in}}(\omega)
\]  
(2.30)

where \(\mathcal{E}_{\text{in}}(\omega)\) is the complex spectral density of the in-going pulses and \(\mathcal{E}_{\text{out}}(\omega)\) is the complex spectral density of the transformed pulses leaving the system. The linear system changes the amplitude of the complex spectral density by the \(S(\omega)\) and introduces the phase-shift \(\phi(\omega)\). Let us suppose that the linear system acts solely in the phase domain. In this case \(S(\omega) = 1\). As result of such transformation the Fourier-limited pulse after the propagation through the linear system receives GVD \(\equiv \phi''(\omega_0)\), TOD \(\equiv \phi'''(\omega_0)\) and higher orders of the linear system phase components. In other words, the pulse will stretch in time via accumulated phase-shifts
while propagating through the linear system. This is illustrated in Fig. 2.17 for the linear system with $S(\omega) = 1$.

![Fig. 2.17 Femtosecond pulse transformation through the linear system](image)

A Fourier-limited pulse stretched by the linear system with a positive (negative) GVD term is called up-chirped (down-chirped)\textsuperscript{73}. The GVD term is responsible for a symmetrical broadening of the pulses whereas the TOD term causes an asymmetrical broadening. Contributions of higher terms than TOD are important only for few-cycles optical pulses\textsuperscript{21,23,186}.

Generation of femtosecond pulses requires a laser medium with a broadband spectral gain like the Ti-doped sapphire crystal. This medium exhibits a sufficiently large emission spectrum to support pulses even less than 10 fs duration\textsuperscript{20}. The principle of femtosecond pulse generation is based on the locking of the phase relationship between different laser modes in a cavity which is random under normal circumstances. To achieve a fixed phase relationship one can use active or passive mode locking techniques\textsuperscript{73}. In most cases the passive Kerr-lens mode locking (KLM) technique\textsuperscript{23,187-190} is used to generate the femtosecond light pulses. An artificially induced perturbation of the laser cavity leads to sudden high intensity fluctuations. Their propagation in the specially designed laser cavity is more favourable due to the Kerr effect and the laser starts pulsed operation. Further amplification of the femtosecond laser pulses without any additive arrangements would lead to a destruction of the laser media and optics due to the very high intensity leading to self-focusing and other nonlinear effects. The chirped pulse amplification\textsuperscript{14,191-207} (CPA) technique tackles this problem of material damage by stretching – “up-chirping” – of the femtosecond pulses before amplification and recompressing – “down-chirping” – of the amplified pulses back to the initial short pulse duration. In detail, the femtosecond pulses from the master oscillator are stretched in an optical device with very high positive GVD – the stretcher. Such long pulses are routinely
amplified in two types of optical amplifiers – regenerative and multipass amplifiers. Regenerative amplifiers consist of an optical cavity with an optical relay being able to confine and release optical pulses within the cavity. In this way one can regulate the number of passes through the amplifying medium. A disadvantage of the regenerative amplifiers is the relatively large GVD and higher dispersion terms leading to an additional hard controllable stretching of the pulses. On the other hand, the multipass amplifiers have very low dispersion but are not flexible in the choice of the number of passes through the amplifying medium which are realized as “optical-bench-fixed” paths multiplexing at small mutual angles in the amplifying medium. After amplification the pulses are recompressed back to almost the original duration by a device with large negative GVD – the compressor.

The high intensities of femtosecond light pulses are predestining them for the stimulation of nonlinear optical effects. Classical nonlinear optics is based on the perturbation theory. At low intensities (\(< 10^{13} \text{ W/cm}^2\)) nonlinear phenomena have been successfully described with the Maxwell equations and a medium polarisation ansatz

$$P = \varepsilon_0 \chi^{(1)}(E)E = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \ldots + \varepsilon_0 \chi^{(n)} E^n$$

(2.31)

where \(\chi^{(n)}\) are known as the nonlinear optical susceptibilities of \(n\)th order. A representative class of the second order nonlinear effects like second harmonic generation, sum frequency mixing, optical rectification, optical parametrical generation are governed by the \(\chi^{(2)}\) susceptibility. Third harmonic generation, self-focusing, two-photon absorption, self-phase modulation are modelled on the \(\chi^{(3)}\) susceptibility. At higher light intensities (\(> 10^{13} \text{ W/cm}^2\)) the light electric field is not merely a small perturbation of the atomic Coulomb potential. To describe the nonlinear effects accompanying such high light intensities one has to perform an \textit{ab initio} quantum mechanical calculation of the system atom and high intensity light field.

The key-process powering all experiments throughout this thesis is the high harmonic generation, theoretically and experimentally explored over one decade now. In this process the high harmonic photons in the VUV, EUV and soft X-ray region are produced by the interaction of the intense laser field (\(>10^{14} \text{ W/cm}^2\)) with an atomic gas. The classical interpretation of the high harmonic generation is based on a three-step model. In the first step, an electron tunnels through the Coulomb barrier suppressed by the intense laser field. Once free, the electron is oscillating and gaining energy from the laser field and under certain
circumstances recombines with the mother ion. The electron recombination process\textsuperscript{209} attends the photon emission with the energies

\[ E_{hh} = n \cdot \hbar \omega \]  

(2.32)

where \( \omega = 2\pi / T \) is the laser field frequency and \( n \) is odd integer number. To estimate the maximum extractable photon energy we can use the classical trajectory\textsuperscript{209,211} \( x(t,t_0) \) of the free electron born at the time \( t_0 \) in the laser field \( \mathcal{E} = E \sin(\omega t) \)

\[ x(t,t_0) = x_0 + \frac{v_0}{\omega} (\sin(\omega t_0) - \sin(\omega t)) + (t - t_0)v_0 \cos(\omega t_0) \]  

(2.33)

The kinetic energy of the oscillating electron in the laser field is then given simply as

\[ E_{kin}(t,t_0) = 2U_p \left[ \cos^2(\omega t) - 2 \cos(\omega t) \cos(\omega t_0) + \cos^2(\omega t_0) \right] \]  

(2.34)

![Fig. 2.18 Kinetic energy (contour plot) and recombination times (shown as white paths) of the free electron born at the time \( t_0 \) in the laser field with period \( T \).](image-url)
where $v_0 = eE/m\omega$ and $U_p = e^2E^2/4m\omega^2$ is the ponderomotive energy of the electron in the laser field. To estimate the maximum energy of the emitted high harmonic photons we have to know the actual kinetic energy of the electron colliding with the mother ion. The contour plot in Fig. 2.18 shows the electron’s kinetic energy $E_{\text{kin}}(t,t_0)$ given by equation (2.34) in the oscillating laser field at arbitrary normalized time $t/T$ born in the laser field $E$ at the normalized time $t_0/T$. Solutions of the equation (2.33) for $x(t,t_0) = 0$ shown in Fig. 2.18 as white “recombination paths” constitute the only possible recombination times for electron with mother ion in the oscillating laser field. The graphical solution (Fig. 2.18) of the electron recombination process makes clear that only electrons born in the second and fourth quarter of the laser field period will return to the mother ion and can radiative recombine. The electrons born in the first and third quarter of the laser field period will never return to the mother ion again and therefore do not contribute to the high harmonic generation (shown by hatched area in Fig. 2.18). The electrons born in the laser field at the times $t_0 = \{0.3T, 0.8T\}$ will return to the mother ion 0.64T period later with the maximum possible kinetic energy $3.17U_p$ obtained in the laser field (shown with the arrow in Fig. 2.18). Radiative recombination for this case constitutes the cutoff energy for the high harmonic photons defined as

$$E_{hh}^{\text{max}} = I_p + 3.17U_p$$

(2.35)

where $I_p$ is the ionization potential of the atomic gas. In the case of a few-cycles light pulses the possibility of a single attosecond pulse generation near the cutoff photon energy has been proposed and recently experimentally confirmed.
Chapter 3

Experimental Setup

3.1 Descriptions of Experimental Setup

The constructed experimental apparatus for photoelectron spectroscopy in the EUV region consists of four main parts (Fig. 3.1):

- femtosecond high-power laser system (0.2 TW)\textsuperscript{45}
- conversion chamber for the high harmonic generation\textsuperscript{45}
- EUV multilayer monochromator with low GVD\textsuperscript{46}
- UHV analysis chamber
Chapter 3 – Experimental Setup

Fig. 3.1 Layout of the built experimental apparatus
In the framework of this thesis, a femtosecond laser system based on the CPA technique has been built\textsuperscript{45}. A scheme of the system is shown in Fig. 3.2., a detailed true-to-scale technical drawing is depicted in Fig. 3.4.

![Diagram of the laser system](image)

**Fig. 3.2 Scheme of the 0.2 TW femtosecond laser system**

The master-oscillator – a KLM Ti:Sapphire femtosecond oscillator\textsuperscript{190} pumped with 3.6 W from a diode-pumped frequency-doubled solid-state laser (Spectra-Physics Millenia) - serves as a seed laser with \(p\)-polarized pulses of 5 nJ energy at a rate of 77 MHz, a bandwidth of 20 nm (FWHM) at a center wavelength of 800 nm, and a pulse duration of 35 fs (Fourier-limited pulse). The pulse spectrum is monitored with a compact Czerny-Turner type spectrometer\textsuperscript{45}. The pulse duration can be measured with a scanning second harmonic autocorrelator\textsuperscript{45}. Complete characterization of the oscillator pulses can be performed with the single-shot second harmonic frequency-resolved optical gating (SHG-FROG) technique\textsuperscript{263}, which is presently in the test stage. Operation in the mode-locking regime is started with a slight reversible disalignment of the laser cavity. This can be observed as a sudden change in the spectrum of the laser pulses. The single line of the continuous mode spectrum is replaced with a broadband spectrum of nearly Gaussian distribution being a signature of the pulsed mode. Once in the pulsed regime, the oscillator runs stable over more than 12 hours with a slight shift of the spectral maximum of the order of 1-2 nm. Maintenance of the oscillator rests upon a small adjustment of the oscillator end-mirror approximately every two months. Femtosecond pulses from the master oscillator enter the pulse stretcher before amplification. Due to high positive GVD the femtosecond pulse duration after passing the stretcher is extended to approximately 220 ps at an energy of 3 nJ. The all-reflective pulse stretcher working in the Littrow configuration\textsuperscript{265} has been designed with particular attention to minimize space requirements. Changing the angle of the stretcher grating also pre-compensates TOD of the following amplification stages. The pulse stretcher is maintenance-free and only precise alignment of the laser beam into the stretcher is required.
The chirped pulses leaving the pulse stretcher are propagating through the polarizer, quartz rotator and Faraday rotator so that the polarization is changed from $p$ to $s$-polarization.

The regenerative amplifier cavity provides high quality only for $p$-polarized light pulses whereas $s$-polarized light pulses are rejected. The Pockels-cell - synchronized with the pump laser and master oscillator - changes the polarization from $s$ to $p$ for a single laser pulse in the regenerative cavity. The confined laser pulse propagates in the cavity and becomes amplified in the Ti:Sapphire crystal pumped with 27 mJ from a frequency-doubled pulsed Nd:YAG laser ($\lambda=532$ nm, Spectra Physics LAB-150-50) at 50 Hz repetition rate. After the pulse amplification saturates, the pulse propagates additional two or three round-trips in the regenerative cavity before the Pockels-cell changes its polarization back to $s$ and the pulse is ejected from the regenerative cavity. The additional round-trips after the saturation are aimed to stabilize pulse-to-pulse energy fluctuations. The amplified pulse propagates back through the Faraday and quartz rotator but in this propagation direction the pulse polarization is not changed and the polarizer redirects the amplified pulse to the multipass amplifier with a pulse energy of about 1.7 mJ. The maintenance of the regenerative amplifier consists mainly of the compensation of a small day-to-day “beam-walk” of the pump laser and tilting of the Pockels-cell. The pre-amplified pulse from the regenerative amplifier propagates in five successive passes through the Ti:Sapphire crystal pumped with 100 mJ from the Nd:YAG
laser. The multipass amplifier boosts the pulse energy up to 20 mJ. The cavity-free design of the multipass amplifier causes its high sensitivity to an optical misalignment. As a result, a complete new alignment of all five passes is necessary once every three months. The last component of the CPA system is an all-reflective pulse compressor working in Littrow configuration with an easily adjustable net negative GVD. After propagation through the pulse compressor the laser pulse has an energy of 15 mJ and a pulse duration about of 70 fs. The less then 100% efficiency of the polarizer in the regenerative cavity gives rise to a leakage of pre-pulses during the amplification. The main pulse and its pre-pulses are shown in Fig. 3.3. The pre-pulse/pulse contrast ratio of 1:85 is typical for normal day-to-day operation. The pulse duration is minimized by means of maximalization of the pulse spectral broadening by the supercontinuum generation\cite{266,267} after focusing the pulse in the air. The whole laser system is situated in a separate air-conditioned room with laminar flow-boxes above the laser bench guaranteeing a particle-free atmosphere.

A detailed down-scaled drawing of the setup for pump-probe experiments is shown in Fig. 3.5. The laser beam is divided with beam splitter into a pump and a probe path with an energy ratio of 3:7. The probe beam is magnified two times with an off-axis reflective Galileo telescope and focused with a lens \((f = 500 \text{ mm})\) into the conversion chamber to an intensity of \(10^{15} \text{ W/cm}^2\) in front of the 0.8 mm diameter nozzle of a pulse valve (Lasertechnics LPV 300) backed with 6 bar of Ne gas. Due to synchronized pulsed operation with an open duration of 145 \(\mu\)s a 330 l/s turbomolecular pump is sufficient to maintain a pressure of \(4 \times 10^{-4} \text{ mbar}\) in the conversion chamber. A 100 nm thin Al filter (Lebow company) as an entrance window to the monochromator chamber reflects the fundamental and low harmonic pulses and acts as a bandpass filter \((T \sim 60\%)\) for high harmonics with the energies between 15 eV and 73 eV. The Al filter is placed on a motorized arm and can be moved in and out of the high harmonics propagation path according to requirements. Under operating conditions the monochromator vacuum chamber, pumped by a 500 l/s turbomolecular pump maintains a pressure of \(1 \times 10^{-6} \text{ mbar}\). A microchannel plate (MCP) intensified phosphor screen can be inserted into the beam path at distance of 1 m from the pulsed valve for visualizing the high harmonics spatial profile. The divergence (full angle) of all high harmonics within the Al-bandpass was measured to be less than 10 mrad. For small fundamental laser energies the high harmonics emission is very directional with a small divergence as can be seen in Fig. 3.6. The conversion efficiency saturates at about 5 mJ of the fundamental laser energy.
Fig. 3.4 True-to-scale technical drawing of the 0.2 TW CPA femtosecond laser system
Fig. 3.5 True-to-scale technical sketch of the visible / EUV pump-probe experiment
Higher fundamental laser energies above 5 mJ result in a spatial distortion of the high harmonic profile as shown in Fig. 3.6 and decreased conversion efficiency as a consequence of an exceedingly high plasma density in the interaction volume which can be easily observed visually as an incoherent plasma radiation.

The multilayer monochromator has to fulfill three basic requirements:

- select a single high harmonic order from the harmonic spectrum while preserving its femtosecond pulse duration – the selecting element must have a small GVD
- refocus the diverging high harmonic beam into a well defined target volume and thus providing a high light intensity
- conserve the propagation direction of the high harmonics

The first requirement has been realized with specially designed molybdenum/silicon multilayer mirrors with 30 periods of 9.9 nm thickness and a narrow bandwidth of about 2.9 eV (FWHM). Given the thickness of a complete multilayer structure of some \( d = 300 \text{ nm} \) one can expect the temporal broadening \( \Delta \tau \) of the pulses not to exceed the time delay between reflection from the multilayer surface and the substrate, respectively \( \Delta \tau < 2d/(c \cdot \cos \theta) \approx 2 \text{ fs} \) where \( c \) is the light velocity and \( \theta \) is the light incident angle. The calculations of the broadening based on the Fresnel-equations actually yields \( \Delta \tau < 1 \text{ fs} \) for a 70 fs EUV pulse.

The second and the third requirement is fulfilled with the Z-fold mirror design where the first multilayer is deposited on a planar substrate and the second one on a concave spherical substrate with a radius of 1 m. The wavelength selective reflection of the multilayer mirrors is ruled by the Bragg condition. By changing the angle of incidence I can select
a narrow energy band and focus it to an area of \( \sim 1 \text{ mm}^2 \) in the UHV experiment chamber. A variable position of both mirrors along the beam direction accomplishes a stable focus location independent on the chosen angle of the multilayers. The currently used multilayer mirrors are tailored for effectively selecting the high harmonics of orders 43, 45, and 47. By changing the set of the multilayer mirrors the tuning range of the monochromator can be extended. A EUV photodiode (XUV-100C, UDT Sensors Inc.) provides routinely control of the photon flux available in the target which is typically \( 10^4 \) photons per laser shot at an energy of 70 eV. The overall transmittance of the multilayer monochromator including Al filter is estimated to be 5% for a single harmonic order.

The pump beam propagates through a delay stage with a translatory precision of 1.2 \( \mu \text{m} \) (\( \sim 4 \text{ fs} \)) and is then imaged onto a BBO crystal (thickness 0.3 mm) with an off-axis reflective Galileo telescope demagnified by a factor of 2.5. The hygrosopic BBO crystal is located in a vacuum steel chamber with Brewster-cut windows to avoid surface deterioration. The second harmonic at 3.1 eV (\( \lambda = 400 \text{ nm} \)) generated in the BBO crystal is focused with a lens (\( f = 4 \text{ m} \)) into the monochromator chamber where two additional mirrors are redirecting the pump beam into the UHV analysis chamber. All mirrors after frequency doubling are wavelength selective for 3.1 eV light energy. I have also performed experiments with a pump photon energy of 1.55 eV (\( \lambda = 800 \text{ nm} \)). In this case the demagnifying optics and the BBO crystal have been removed and all the mirrors after the BBO crystal have been exchanged according to the fundamental light energy.

The radiation of a selected high harmonic probe pulse together with a temporally delayed pump pulse are spatially overlapped at an angle of 12 mrad onto a target in the UHV chamber. The differential pumping stage bridging the pressure difference between the monochromator and the experiment chamber consists of two apertures and a 210 l/s turbomolecular pump. On demand, removing the Al filter in the monochromator and moving a bending mirror into the pump and probe path allows an imaging of the interference pattern of both pump and probe pulses on a CCD camera for in situ calibration of the time delay. With this technique I can set equal optical paths for pump and probe pulses. In this case to avoid multilayer degradation I use only unamplified femtosecond pulses directly from the master oscillator which provides me also with a better signal statistics due to its high repetition rate. When the second harmonic is used as pump pulse the additional BBO crystal (thickness 0.1 mm) is introduced into the optical path of probe pulses. Correspondingly, a blocking filter for the fundamental light is placed in front of the CCD camera and only interference on the second harmonic is observed. After finding equal optical lengths for pump
and probe paths I have to correct this value by the optical thickness of the BBO crystal with respect to vacuum (~166 fs). Finally the Al filter is moved back to its original position and despite small readjustments required before running the pump-probe experiment the pump-probe temporal coincidence is stable within about 100 fs for a few days.

The observation of the interference pattern of pump and probe pulse is also informing about possible wave-front deformations and the influence of dispersive optical elements in the optical paths deteriorating the interference contrast. In Fig. 3.7 the interference of pump and probe pulses with photon energy 1.55 eV is shown. A linear variation of the interference maximum-to-maximum spacing is giving information on the wave-front tilt. This is to be expected because of the astigmatic optical setup of the multilayer mirrors in the monochromator. Graph in Fig. 3.7 shows the mean value of the interference pattern modulation for a horizontal line-scan in the middle of the interference spot as a function of time-delay between pump and probe pulses. Assuming two identical gaussian Fourier-limited pump and probe pulses with an intensity profile defined as $I(t) = E(t) \cdot E(t)^* = I_0 \exp(-4 \ln 2 \cdot t^2 / \tau^2)$, the acquired pump-probe coherence function $\Gamma(t)$ representing the $E$-field autocorrelation is given as\textsuperscript{272,273}

\textsuperscript{8} The calculated normal reflectivity\textsuperscript{62} of the topmost Si layer of the multilayer mirror is 35% at 800 nm and 47% at 400 nm light wavelength.
yielding the relation $\tau_a = 2\tau$ where $\tau_a$ (FWHM) is the measured width of the autocorrelation function $\Gamma(t)$. The measured autocorrelation width of $\tau_a = 94$ fs then yields a pulse duration of $\tau = 47$ fs, which matches the pulse duration of 45 fs determined with the SHG autocorrelator quite well. This result ascertains that both pump and probe optical paths do not contain optical elements with considerable dispersion. Also the astigmatism resulting from the monochromator mirrors setup is not critical for pump-probe experiments.

\begin{equation}
\Gamma(t) = \int_{-\infty}^{\infty} E(\zeta)^2 \cdot E(\zeta - t) d\zeta \approx \exp\left(-4\ln 2 \cdot \frac{t^2}{(2\tau)^2}\right)
\end{equation}

Fig. 3.8 Selectivity of the multilayer monochromator vs. photon energy of the high harmonics and the angle of incidence of the multilayer mirrors. The inset shows monochromator layout.

The UHV experimental chamber has a base pressure of $3 \times 10^{-10}$ mbar rising to $9 \times 10^{-10}$ mbar when operating the Ne gas jet in the conversion chamber and is equipped with the standard surface preparation equipment and analysis methods such as an ion bombardment gun, low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and quadrupole mass analyzer (QMA). As targets solid samples as well as gases can be investigated. The position of the selected high harmonic within the chamber is controlled with a quadrant metal photocathode intensified with a microsphere plate (MSP). In gas phase experiments the low 50 Hz repetition rate of the laser system enables usage of the
synchronized pulsed valve providing a high local target gas density in front of the electron spectrometer at low background pressure (10^{-6} mbar). Due to an unfavorable duty cycle of the piezo-driven pulsed valve, such technique becomes less efficient with high repetition rate (kHz) laser sources. For energy analysis of photoelectrons or Auger electrons excited with the high harmonic pulses a time-of-flight (TOF) electron spectrometer is used\(^4\). A benefit of the TOF technique is its capability to simultaneously analyze electrons of different kinetic energies. An electrostatic lens system at the entrance of the μ-metal shielded electron drift-tube (length 40 cm) lets me dynamically modify the acceptance solid angle of the TOF spectrometer from 0.06% to 5% of 4\(\pi\) at the expense of energy resolution. To achieve better resolution at electron kinetic energies >20 eV a retardation voltage has been applied. The time-resolved electron signal detected on a 40 mm diameter MSP detector is transmitted to a discriminator (Philips Scientific, Model 6904) followed by a fast multiscaler (FAST, Model 7886) with 0.5 ns time resolution. A digitizing oscilloscope (Tektronix DSA 602) proved to be useful for alignment purposes.

As mentioned, the main challenge in the selection of a single harmonic order from the high harmonics spectrum driven by 1.55 eV femtosecond pulses is to achieve sufficient contrast between the desired high harmonic and the neighboring odd orders. I have used photoionization of He gas as a precise and convenient method to measure the selectivity of the multilayer monochromator\(^{45,46}\). If only one particular high harmonic is selected, only a single photoelectron peak with the energy \(h\nu - I_p\) is observed in photoelectron spectrum, where \(h\nu\) is the photon energy and \(I_p = 24.6\) eV is the first ionization potential\(^{283}\) of He. Hence, the photoelectron spectrum of He gas directly reflects the spectral distribution of the exciting radiation. The measured selectivity of the monochromator for systematically varied angles of the multilayer mirrors is shown in Fig. 3.8. By changing the multilayer angle of incidence between 11 and 26 degrees selection of one high harmonic with a photon energy between 66 eV and 73 eV has been performed. A strong absorption\(^{274}\) at the Al L\(_{2,3}\) -edge leads to the small observed intensity of the high harmonic at 73 eV photon energy. The highest selectivity has been achieved for 70 eV photon energy corresponding to an angle of 20 degrees. The contrast ratio to the neighboring high harmonics at 70 eV is measured to be better than 1:10. Recently, it has been shown that the yield of one specific high harmonic can be optimized through the variation of the driving pulse phase\(^{255,276}\). Applying this technique\(^{275}\) would enhance the contrast ratio between the selected and adjacent high harmonics.

The temporal stability of the 45\(^{th}\) high harmonic measured as total photoelectron yield from GaAs target is shown in Fig. 3.9. It depends on the laser system stability which is a
function of the pump laser pointing stability. Summary of the femtosecond CPA laser system and the high harmonic femtosecond EUV source is given in Tab. 3.1. Detailed description of the photon flux measurement at 70 eV photon energy and the estimation of the EUV pulse spectral bandwidth is given in Ref. 45. The EUV pulse duration of 70 fs has been measured by means of time-resolved photoelectron spectroscopy on Pt surface (see section 5.2). The EUV focus size before the entry aperture of the TOF electron spectrometer has been measured with the knife-edge technique (Appendix A). The polarization of high harmonics is the same as the polarization of driving laser.

Fig. 3.9 Measured temporal stability of the 45th high harmonic over four hours

<table>
<thead>
<tr>
<th>fs - lasersystem</th>
<th>fs - EUV radiation</th>
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<tbody>
<tr>
<td>energy</td>
<td>tuneability</td>
</tr>
<tr>
<td>wavelength</td>
<td>photon counts</td>
</tr>
<tr>
<td>duration</td>
<td>pulse duration</td>
</tr>
<tr>
<td>rep. rate</td>
<td>bandwidth</td>
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<td></td>
<td>polarisation</td>
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<tr>
<td></td>
<td>focus size</td>
</tr>
<tr>
<td>15 mJ</td>
<td>66.8 - 73 eV (present ML)</td>
</tr>
<tr>
<td>800 nm</td>
<td>10^4 photons per pulse</td>
</tr>
<tr>
<td>70 fs</td>
<td>femtosecond (&lt; 70 fs)</td>
</tr>
<tr>
<td>50 Hz</td>
<td>&lt; 300 meV</td>
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<td></td>
<td>linear</td>
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<td>~ 1.2 mm</td>
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Table 3.1 Summary of the properties of the CPA fs-laser system and fs-EUV source.
Chapter 4

Test Measurements

4.1 Photoelectron Spectroscopy on Metals, Semiconductors, Adsorbates and Gases

High harmonics proved to be efficient tools for the static photoelectron spectroscopy although the repetition rate of the high harmonic sources is $10^5$ times smaller than that of the storage rings. The first application of high harmonics as a compact table-top equivalent of storage rings in the EUV region was demonstrated by Haight et al.$^{120,121}$ Availability and easy operation of the high harmonic sources$^{279}$ made systematic and extremely time consuming studies possible. This has lead to detailed studies of the electronic structure of metals and their adsorbates$^{277,278}$.

To illustrate the capability of my system to obtain well resolved photoelectron spectra, I have recorded the photoelectron spectrum from the Pt(110) surface shown in Fig. 4.1. The Pt crystal has been cleaned with acetone before transfer to the UHV vacuum chamber. In vacuum it has been cleaned with the Ar$^+$ ion bombardment (1.6 keV), heating (630 K) in an oxygen atmosphere (8x10$^{-8}$ mbar) and flashing (1000 K). The cleanness has been confirmed with an Auger electron spectrum which was free of all contamination (Appendix B – Fig. B.1). The proper surface reconstruction has been verified with LEED which displayed well ordered (1x2) surface reconstruction$^{280,281}$. 
Fig. 4.1 Photoelectron spectrum of the Pt(110) crystal excited with the 45th high harmonic.

Fig. 4.2 Photoelectron spectrum of the p-GaAs(100) crystal excited with the 45th high harmonic.
The photoelectron spectrum excited with the high harmonic of 70 eV photon energy shows a dominant and well resolved Pt valence band. In order to increase the energy resolution of the TOF spectrometer the retarding voltage of 35 V has been used. The light of 70 eV photon energy generates core-holes in the 5p\(_{3/2}\) (E\(_{\text{bin}}\) = -51.7 eV) and 5p\(_{1/2}\) (E\(_{\text{bin}}\) = -65.3 eV) states. The kinetic energy of the 5p\(_{3/2}\) photoline excited with the 70 eV photon energy is only 12.9 eV and has not been detected with the used retarding voltage. The photoemission from the 5p\(_{3/2}\) state with 70 eV photon energy has enhanced cross section (see equation (2.4)) due to the high density of final states between 18 eV and 20 eV above the Fermi niveau. The O\(_3\)VV Auger electrons resulting from the 5p\(_{3/2}\) core-hole decay are therefore well pronounced.

The photoelectron spectrum of the p-GaAs(100) crystal is shown in Fig. 4.2. The retarding voltage of 5 V has been used. The GaAs crystal has been cleaned in toluene, acetone, tricholoethylene, acetone and ethanol before transfer into vacuum. In vacuum a clean p-GaAs(100) surface has been achieved with repeated cycles of sputtering with 1.5 keV Ar\(^+\) ions and annealing at 500 °C. After such preparation the Auger electron spectra showed no carbon and oxides contamination (Appendix B – Fig. B.3). The GaAs(100) surface exhibits a variety of reconstructions which are conveniently recognized observing the photoline intensity ratio Ga-3d/As-3d. The photoelectron spectrum clearly resolve Ga-3d and As-3d photolines. The Ga-3d photoemission cross section has a maximum for 70 eV photon energy and the photoelectrons emitted from the surface exhibit maximum surface sensitivity. The inset of the Fig. 4.2 shows the As-3d resolved spin-orbit splitting of 0.7 eV. The photoemission cross section for the GaAs valence band at 70 eV photon energy is more than one order of magnitude smaller as compared to the Ga-3d cross section. The measured selectivity ratio of the 45\(^{\text{th}}\) to 47\(^{\text{th}}\) high harmonic is about 6%. This can be further reduced to a virtually pure single high harmonic under the special circumstances shown later in Fig. 6.4.

To demonstrate the capability of the built apparatus also the photoelectron spectra of adsorbates have been measured. Fig. 4.3(b) shows the photoelectron spectrum of wolframhexacarbonyl W(CO)\(_6\) adsorbed on a Si(100) surface together with the W(110) photoelectron spectrum (Fig. 4.3(a)) for comparison. The TOF retarding voltage of 0 V has been used. The W(110) crystal has been cleaned by several flashing and oxidation cycles.

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\(^{1}\) The kinetic energy of electron throughout this thesis is refereed to the electron’s kinetic energy direct after emission from the target and not after the retardation in the TOF spectrometer.

\(^{2}\) The work function of Pt(110) (1x2) surface is 5.4 eV.
Fig. 4.3 Photoelectron spectra of the W(110) crystal (a) and W(CO)$_6$ adsorbate (b)

Fig. 4.4 Photoelectron spectrum of Ga$_3$. The UPS spectrum is taken from Ref. 307.
Surface cleanliness has been confirmed by the observation of well pronounced 4f\textsubscript{5/2} and 4f\textsubscript{7/2} photolines in the photoelectron spectrum (Fig. 4.3(a)) which are surface sensitive. On the basis of known values of the binding energies\textsuperscript{283,301-303} for 4f\textsubscript{5/2} (E\textsubscript{bin} = -33.6 eV) and 4f\textsubscript{7/2} (E\textsubscript{bin} = -31.4 eV) states the photoelectron spectrum has been converted to the electrons’ binding energies to make the direct comparison with W(CO)\textsubscript{6} possible. The W 4f binding energies in Ref. 283 are given with the accuracy of ±0.1 eV which sets the upper limit on the chemical shift error evaluation although the peak position for the W 4f\textsubscript{5/2} is determined by the fitting with Gauss function with an error of 10 meV. The W(CO)\textsubscript{6} has been evaporated onto Si(100) surface terminated with an OTS (Octadecyltrichlorosilane) self-assembled monolayer\textsuperscript{305} with the Si(100) substrate held on -100°C with a liquid nitrogen cooler. After evaporation the W(CO)\textsubscript{6} adsorbed layer could be observed visually as the reflectivity of substrate had changed. The adsorbed W(CO)\textsubscript{6} photoelectron spectrum (Fig. 4.3(b)) shows well resolved molecular orbitals belonging to the CO groups\textsuperscript{298-300} as well as both core-level 4f lines. The photoelectron spectrum has been converted to the electrons’ binding energies on the knowledge of the CO groups position\textsuperscript{298}. The distinctive chemical shift\textsuperscript{304} ∆E\textsubscript{EC} = 1.2 eV of 4f core-levels points on the different electronic environment of the W atoms in the W(110) surface and the W(CO)\textsubscript{6} adsorbate, respectively. This demonstrates the usefulness of this apparatus for electron spectroscopy for chemical analysis (ESCA) in the EUV region.

Recently the technical relevance of the organic materials\textsuperscript{306} for light-emitting diodes was recognized. One of the promising and extensively studied materials is tris(8-hydroxyquinolinato) gallium (Ga\textsubscript{3})\textsuperscript{307-313}. Fig. 4.4 shows the photoelectron spectrum of Ga\textsubscript{3}. The TOF retarding voltage of 30 V has been applied. The Si(100) crystal has been stripped of its natural oxide layer in a buffered HF solution and transferred into the vacuum chamber where it was cleaned with heating cycles up to 830 °C. For the evaporation\textsuperscript{314} of Ga\textsubscript{3} a Al\textsubscript{2}O\textsubscript{3} single-ended tube (Friatec AG) resistively heated with molybdenum wire has been used at temperatures up to 280 °C. The presence of a Ga\textsubscript{3} film has been checked as a visual change in the substrate reflectivity. The photoelectron spectrum in Fig. 4.4 shows the well resolved Ga\textsubscript{3} molecular orbitals excited with 70 eV photon energy together with a spectrum measured with He I-UPS for comparison\textsuperscript{307}. The Ga-3d core-level photoline in Fig. 4.4 points to the excellent sensitivity of this measurement method for a single atomic species embedded in a large molecular complexes.
Fig. 4.5 Photoelectron spectrum of I$_2$ adsorbate excited with the 45$^{th}$ high harmonic after subtraction of the secondary electron background. The inset shows the originally measured spectrum.

Fig. 4.6 Photoelectron and Auger spectrum of Xe after photoionization with 73 eV.
I have also investigated the photoelectron spectra of iodine films with the objective of Auger 4d core-hole decay observation. Iodine films have been prepared by condensing $\text{I}_2$ molecules from an electrochemical AgI cell onto Si(100) surface terminated with OTS self-assembled monolayer cooled with liquid nitrogen to $-100 \, ^\circ\text{C}$. The photoelectron spectrum of an $\text{I}_2$ adsorbate excited with 70 eV photon energy is shown in Fig. 4.5. The TOF retarding voltage of 0 V has been used. The iodine $4d_{3/2}$ and $4d_{5/2}$ photolines are obscured with a massive secondary electron background as shown in inset of Fig. 4.5. Double-exponential background subtraction reveals both 4d core-level photolines. The measured spin-orbit splitting is $\Delta E_{FS} = 1.7 \, \text{eV}$. The N$^{4,5}$O$^{2,3}$O$^{2,3}$ Auger decay of the 4d core-hole is observed as a broad less prominent feature between 20 eV and 30 eV kinetic energy.

The first measurements, however, were performed in the gas phase photoionizing He for spectral characterization of the multilayer monochromator (see section 3.1). For completeness, Fig. 4.6 shows the photoelectron and Auger spectra of Xe gas after the photoionization with 73 eV photon energy and TOF retarding voltage of 15 V. The photoionization of the 5s and 5p shells gives rise to the photoelectron peaks at energies 49.5 eV and 61 eV, respectively. Increasing the retardation voltage of the TOF spectrometer to 35 V and using the photon energy of 70 eV, I can observe the spin-orbit splitting of the 5p energy level (inset in Fig. 4.6). The photon energy of 73 eV is sufficient to create a hole state in the 4d shell which relaxes through the characteristic NOO Auger decay. Electrons corresponding to the N$^{4,5}$O$^{2,3}$O$^{2,3}$ Auger decay as well as 5s-satellites are well distinguished in the electron spectrum. The measured linewidth of 0.9 eV (FWHM) of the Auger electron peak N$^{5}$O$^{2,3}$O$^{2,3}$ ($^{1}\text{S}_{0}$) is considerably larger than the natural linewidth of 120 meV. Since Auger linewidths are generally independent on the bandwidth of the exciting radiation, this value represents the energy resolution of the TOF spectrometer at 30 eV electrons’ kinetic energy and 15 V retardation potential. The variation of the TOF energy resolution has been analyzed in Ref. 45 in detail. Taking into account the limited resolving power, the photoelectron and Auger electron spectrum are in reasonable agreement with spectra measured with synchrotron radiation.
5.1 Measurement of Hot Electrons on a Pt(110) Surface

The idea of the experiment is based on the photoexcitation of electrons from occupied states of the valence band into unoccupied states above the Fermi level with a visible pump pulse. These excited short-lived electrons (see section 2.1.2) (also called “hot electrons”) are then emitted with an EUV probe pulse into vacuum where they are energy-analyzed. The time delay between pump and probe pulses can be continuously changed. In this way, I obtain information on the transient population above the Fermi level at the surface. The implementation of the principle for the Pt(110) surface is shown in Fig. 5.1. The pump pulse with 1.5 eV photon energy and 70 fs duration excites electrons from occupied d-band states in the valence band into unoccupied states above the Fermi level as shown in the energy-time representation in Fig. 5.1(a).
Fig. 5.1 Principle of the visible-pump/EUV-probe hot electron spectroscopy on a Pt surface shown in (a) energy-time representation and (b) space-time representation.
The total absorbed light intensity of $1.6 \times 10^{11}$ W/cm$^2$ excites 2.2% of all valence band electrons. These hot electrons relax very rapidly via e-e scattering. It has been shown that the hot electron’s life times of transition metals are remarkably shorter than the life times of noble metals. This phenomenon is due to the large phase space for e-e scattering caused by the high density of states (d-band) at the Fermi edge. On the contrary, totally filled d-bands of the noble metals and solely contribution of the s-bands to the e-e scattering at the Fermi edge are responsible for the relatively long-lived hot electrons. The probe pulse with a photon energy of 70 eV and duration of less than 70 fs projects the current electron distribution into the vacuum as shown in Fig. 5.1(a). Changing the time delay between pump and probe pulses I can track the temporal evolution of the electronic population at the Fermi edge. Here I define the time delay as positive when the pump pulse precedes the probe pulse. The kinetic energy of the hot electrons emitted with the probe pulse is about 65 eV. Such electrons are mainly (86% of all registered electrons) originating from only 0.88 nm depth. At this point I have to assume also a ballistic transport (1 nm/fs) and a diffusion (10 nm/ps) of hot electrons from the probe spot at the surface (Fig. 5.1(b)). Consequently, the net observed relaxation times of hot electrons at Pt surface is expected to be smaller than 3 fs for the hot electrons of 1.5 eV kinetic energy with respect to the Fermi niveau.

I have used a variant of the experimental setup shown in Fig. 3.1 without the frequency doubling unit for pump pulses. In this experiment the repetition rate of the laser system was 10 Hz and the time-resolution of used TOF electron detection system was 1.5 ns. The clean Pt(110) surface has been prepared as described in section 4.1. The $p$-polarised pump pulses (800 nm, 1.55 eV) with energy 0.5 mJ and duration of 70 fs were focused together with the 70 eV $p$-polarised probe pulses on the Pt(110) surface. The pump and probe incident angle measured from the surface normal was 53°. The axis of the TOF spectrometer and surface normal made an angle of 8° and the retardation voltage was 35 V. The photoelectron spectra for –400 fs, 0 fs, and +400 fs delay are shown in Fig. 5.2. The photoelectron spectra for ±400 fs are identical in the region above the Fermi level indicating that hot electrons for +400 fs are complete thermalized. The photoelectron spectrum for time delay 0 fs shows a clear deviation when compared with the spectra for ±400 fs. When pump

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8 Total number of absorbed photons $N_A = 8.4 \times 10^{14}$ is given by $N_A = (1-R)N_I$ where $N_I = 2 \times 10^{15}$ is the number of incident photons and $R = 0.58$ is the reflectivity of Pt for the incident angle 53° and photon energy 1.55 eV. The 86% of all photons are absorbed in the depth of 26 nm. The pump spot at the surface was $19 \times 10^{-3}$ cm$^2$, resulting in total excited electron density of $1.5 \times 10^{22}$ cm$^{-3}$. The electron density of Pt valence band (5d, 6s electrons) is $6.6 \times 10^{23}$ cm$^{-3}$, yielding the net valence band electronic excitation of 2.2%. 

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and probe pulses hit the Pt surface in temporal coincidence I have to observe the highly non-equilibrium electron distribution above the Fermi edge. This has been observed as shown in the inset of Fig. 5.2. The probe pulse with 70 eV photon energy creates a core-hole in the 5p\(^{3/2}\) niveau. This core-hole relaxes as shown in section 4.1 via Auger decay seen as an O\(_{3}\)VV Auger peak on the top of a secondary electron background. The relation between the O\(_{3}\)VV peak shape and the valence band density of states (DOS) is not elementary and in the first approximation is given by the self-convolution of the valence DOS\(^{327-330}\).

Fig. 5.2 Photoelectron and Auger electron spectra of Pt(110) surface for 0 fs and ±400 fs delays between pump and probe pulses.
Naively, one would expect a simple broadening of the O$_3$VV peak due to new possibilities in the Auger recombination process connected with the transient hot electron distribution in the normally unoccupied states above the Fermi level. As shown in the inset of Fig. 5.2, the O$_3$VV Auger peak shifts to lower kinetic energies. A detailed theoretical study of this phenomenon is necessary to account for the observed O$_3$VV Auger peak shift. In the following I will concentrate exclusively on the hot electron dynamics at the Fermi edge which gives more transparent and easily interpretable results. More detailed photoelectron spectra for the three delay times 0 fs and ±100 fs at the Pt Fermi edge measured with the retardation voltage of 45 V are shown in Fig. 5.3. A considerable non-equilibrium electron population above the Fermi edge is present at zero time delay. The spectrum for +100 fs shows no signs of hot electrons above the Fermi edge revealing a very fast hot electron thermalization as expected. The inset of the Fig. 5.3 shows the photoelectron spectrum generated exclusively with the pump pulses which can be attributed to multiphoton emission processes at such high pump intensity. Only by using probe photons with energies exceeding 40 eV the photoelectron signal can be prevented from being obscured by these background electrons. I attribute the observed time-dependent spectral variation of the photoelectron signal at the Pt Fermi edge to a transient hot electron population rather than to a space-charge broadening.
induced by the high local electron density because i) the distinct spectral feature observed at 65.5 eV in Fig. 5.3 does not indicate a simple broadening of the Fermi-edge and ii) due to a velocity of <3.5 µm/ps for electrons with energies lower than 35 eV I would not expect an ultrafast space charge relaxation. A more detailed discussion on the space-charge phenomena is given in section 6.1.

Fig. 5.4 Contour plot of the photoelectron yield vs. kinetic energy and time delay between pump and probe pulses measured at the Pt(110) surface. The time-resolved signal at photon energy 65.5 eV (dashed line) is shown in Fig. 5.8.

A contour plot of the photoelectron yield vs. kinetic energy and time delay between pump and probe pulses (Fig. 5.4) exhibits a fast relaxation of the hot electrons within 100 fs. The data were acquired in four subsequent runs with 96 min duration, each. During this time, no significant changes in the temporal structure of the spectra has been observed. For large negative time delays (<-100 fs) when the probe pulse precedes the pump pulse the measured photoelectron spectra reflect the non-disturbed Fermi edge. For large positive delays (>+100 fs) the hot electron population has already decayed and the measured photoelectron spectra are same above the Fermi edge as the spectra for large negative time delays. For time delays between ±100 fs I observe a symmetrical hot electron distribution above the Fermi
edge with respect to zero time delay. When I assume the temporal profile to be a delta-like function for pump and probe pulses one has to observe the exponentially decreasing hot electron distribution for positive time delays with a maximum for zero time delay. For negative time delays there should be no hot electron population. Consequently, this pump-probe method is not symmetrical for time delay inversion. The actually measured symmetrical distribution for time delays between ±100 fs is caused by the finite time duration of pump and probe pulses which is considerably larger than the characteristic hot electrons life times (see equation (2.27)). This means that the measured hot electron distribution is proportional to the cross-correlation between pump and probe.

![Fermi edge time-resolved photoelectron spectra for the Pt(110)](image_url)

The decrease of the time-resolved photoelectron yield for the electron energies lower than 64 eV (representing the Fermi edge), correlated with the hot electron population, can be understood as an electron depletion of the valence band. At the absorbed intensity of 1.6x10^11 W/cm^2 I deal with a photoexcitation of 2.2% of all valence band electrons. Even larger photoexcitation can lead to the short time scale destabilization of the crystal structure. This in turn can be observed as an alteration of the metal dielectric function. There are also theoretical studies for semiconductors where the photoexcitation of 10% of all valence band electrons leads to collapse of the electronic structure observed as semiconductor band-gap collapse, semiconductor-to-metal
transition, and structural changes leading to an ultra-fast femtosecond melting of the semiconductor. This is the first direct study of the hot electron population and valence band changes at such high pump intensities. The traditional studies\textsuperscript{79} have been performed at intensities more than 10 times lower than in this case. The used pump intensity in my study is still considerably lower than the threshold for plasma formation at metal surfaces\textsuperscript{332} of $10^{13}$ W/cm$^2$.

![Photoelectron spectra near the Pt Fermi edge before and after photoexcitation](image)

Fig. 5.6 Photoelectron spectra near the Pt Fermi edge before and after photoexcitation

Upgrading of the laser system to a repetition rate of 50 Hz has lead to a faster data acquisition. Additionally, a better time-resolution of the TOF electron detection system of 0.5 ns enabled to do the same experiment on the Pt(110) surface with shorter accumulation times and better photoelectron energy resolution. The measured time-resolved photoelectron spectra are shown in Fig. 5.5. The shown spectra have been measured in two sequential runs, each of 52 min duration. The Fermi edge at zero time delay shows the highly non-equilibrium hot electron distribution. The e-e scattering is leading to the hot electron thermalization within few femtoseconds. However e-p interactions occur on a time scale up to a few picoseconds leading to lattice heating (see Fig. 2.8) resulting in a less pronounced – less sharp Fermi edge\textsuperscript{61}. The photoelectron spectra showing the Fermi edge region of the Pt valence band before and after photoexcitation are shown in Fig. 5.6. The observed difference in the photoelectron spectra is not due to a high harmonic intensity drop off, because the shown spectra were acquired in two sequential runs and have been normalized so that the integral of
all registered photoelectrons for all spectra is constant. I therefore associate the observed difference at the Fermi edge with the growing lattice temperature after photoexcitation.

### 5.2 Pump-Probe Cross-Correlation in the EUV Region

The measurement of femtosecond (or even attosecond) pulse duration in the EUV region represents a great experimental challenge. In the infrared, visible and ultraviolet traditional techniques based on nonlinear effects are used for the pulse duration measurement yielding not only amplitude, but also phase information. The current EUV pulse intensities are not high enough to make nonlinear effects observable. Accordingly, the autocorrelation techniques based on nonlinear effects are not available. The tendency is to use instead cross-correlation techniques with a high-intensity visible or infrared “dressing” pulse and an EUV pulse in an experimental setup with a generalized scheme like in Fig. 5.7.

![Fig. 5.7 Scheme of the “dressing-pulse” cross-correlation techniques in the EUV region](image)

One measures photoelectron or Auger electron spectra of the noble gases as a function of the time delay between ionizing EUV pulse and “dressing” pulse with an intensity higher than $10^{11}$ W/cm$^2$. The photoelectron spectrum in the presence of the strong “dressing” pulse field exhibits side-bands of photoelectron peaks as well as peak’s broadening and shifting. This technique has been successfully applied even to the measurement of the trains of attosecond pulses and single attosecond pulses as well. Assuming chirp-free EUV pulses one can estimate their duration also with linear effects like interference. However, daily usage of the femtosecond pulses for the time-resolved spectroscopy in the EUV region is calling for a UHV compatible measurement method utilizing lower intensities than $10^{11}$ W/cm$^2$. The cross-correlation method utilizing the ultrafast relaxing hot electrons on
transition metal surfaces seems to be very efficient and reliable tool for the measurement of femtosecond EUV pulses.

In the section 5.1 I have shown the measurement of a very fast decaying hot electron distribution at the Fermi edge of the Pt(110) surface. The measured transient signal from the hot electron distribution does not allow extraction of the hot electron’s life-times of some few femtoseconds but is proportional to the pump-probe cross-correlation. Let us consider hot electrons with a kinetic energy of 1.5 eV referring to the Fermi level photoexcited with the pump pulse modeled by the gaussian intensity profile \( I_{pu} = I^0_{pu} \exp(-4\ln(2) \cdot \tau^2 / \tau^2_{pu}) \). The photoemission of these hot electrons into vacuum with the EUV probe pulse with the intensity profile defined as \( I_{pr} = I^0_{pr} \exp(-4\ln(2) \cdot \tau^2 / \tau^2_{pr}) \) results in a photoelectron signal depending on the time delay between pump and probe pulses. The photoelectron signal at the kinetic energy of 65.5 eV corresponding to these hot electrons is shown in Fig. 5.8. This signal corresponds to a line-scan shown through the contour plot in Fig. 5.4. Assuming that the registered photoelectrons are governed by the Poisson probability distribution the error bars in Fig. 5.8 show the standard deviation \( \mu \) of the measured photoelectron counts supposing these to be the mean value. The evaluated FWHM error of the cross-correlation signal is given as the standard deviation of the Gauss function width fitting parameter.

Under the approximation of a delta-like fast hot electron relaxation the measured cross-correlation signal \( S(\tau) \) as a function of time delay \( \tau \) between pump and probe pulses is given as

\[
S(\tau) = \int_{-\infty}^{\infty} I_{pu}(\zeta) I_{pr}(\zeta - \tau) d\zeta \approx \exp(-4\ln(2) \cdot \tau^2 / (\tau^2_{pu} + \tau^2_{pr}))
\]

(5.1)

On the basis of this result the measured square of FWHM of the cross-correlation signal is proportional to the sum of the pump and probe pulse duration (FWHM) squares. The measured pulse width of the pump pulse\(^45\) of 70 fs and the cross-correlation width of 100 fs yield the EUV probe pulse duration of approximately 70 fs neglecting the hot electron lifetime. A spectral and spatial drift of the driving femtosecond laser and mechanical system instabilities over the long photoelectron spectra acquisition times have been slightly reduced

\( \mu \) is the mean of the Poisson probability distribution the standard deviation is given by \( \sqrt{\mu} \)
utilizing a new pump laser of 50 Hz resulting in the shorter width of cross-correlation signal show in Fig. 5.8(b).

An application of this method for pulse duration measurements in the EUV region has the following advantages:

- reduced pump intensity of one or two orders compared to the “dressing” pulse intensity higher than $10^{11}$ W/cm$^2$ necessary in gas-phase cross-correlation
- UHV compatible environment during the measurement compared to the some $10^{-4}$ mbar in the “dressing” pulse cross-correlation methods

Fig. 5.8 Cross-correlation of pump and probe pulses corresponding to hot electrons with a kinetic energy of 1.5 eV above the Fermi level as measured with (a) 10 Hz and (b) 50 Hz laser system.
Until now, I have supposed an instant hot electron relaxation but remembering the finite relaxation times of hot electrons restricts this method to measurements in the femtosecond region. But the perspective of higher excitation energies of some 3–4 eV of the pump pulse is leading to even shorter hot electron relaxation times which can push the applicability of this method even to the femto-atto-second edge.
Chapter 6

Time-Resolved Photoelectron Spectroscopy on GaAs(100) Surfaces

6.1 Measurements of Transient Ga-3d Core-Level Shifts on GaAs(100) Surfaces

The principle of the pump-probe measurement used throughout this section is shown in Fig. 6.1. The pump pulse (3.1 eV) with an intensity of $1 \times 10^{10}$ W/cm$^2$ generates approximately $1.6 \times 10^{20}$ cm$^{-3}$ electron-hole pairs in the SCR at the p-GaAs(100) surface. The SCR electric field of few hundreds of kV/cm separates generated electron-hole pairs in less than 1 ps. The electrons drifting to the surface partially compensate the SCR electric field which is leading to the bands flattening. The core-levels are bending in the same manner and with the same amplitude as conduction and valence bands. The time-delayed probe pulse with energy of 70 eV emits the electrons from the Ga-3d core-level into vacuum.

\[^{\S} \text{Total number of absorbed photons } N_A = 1.25 \times 10^{13} \text{ is given by } N_A = (1-R)N_I \text{ where } N_I = 3.14 \times 10^{13} \text{ is the number of incident photons and } R = 0.6 \text{ is the reflectivity}^{362} \text{ of GaAs for the incident angle } 53^\circ \text{ and photon energy } 3.1 \text{ eV. The } 86\% \text{ of all photons are absorbed}^{362} \text{ in the depth of } 30 \text{ nm. The pump spot at the surface was } 23 \times 10^{-3} \text{ cm}^2, \text{ resulting in total } \text{excited electron-hole density} \text{ of } 1.6 \times 10^{20} \text{ cm}^{-3}. \text{ The electron density}^{365} \text{ in GaAs valence band is } 2 \times 10^{23} \text{ cm}^3, \text{ yielding the } \text{net valence band electronic excitation} \text{ of } 0.1\%.\]

Fig. 6.1 Principle of the band-bending after photoexcitation detected by measuring the kinetic energy of the photoelectrons from the Ga-3d shell.
Accordingly, the kinetic energy of Ga-3d photoelectrons is shifting by the same amount as that of valence bands. The Ga-3d photoelectrons’ shifts are therefore giving information on the band-bending as a function of time delay between pump and probe pulses. The surface carrier recombination leading to band-bending receding to the original value is observed as the back-shift of the Ga-3d photoelectrons’ kinetic energy. The high excitation intensity of the pump pulses is giving rise also to multiphoton processes seen as a low-energetic electron tail. The kinetic energy of the Ga-3d photoelectrons emitted with photons of 70 eV energy retains maximal surface sensitivity of circa 1 nm depth.

![Graph showing photoelectrons excited through multiphoton processes](image)

**Fig. 6.2** Photoelectrons excited through multiphoton processes with a pump pulse (3.1 eV) of intensity 10 GW/cm² from the p-GaAs(100) surface

Before discussing the experimental results on transient changes in the SPV at the GaAs surface I elucidate some particular challenges connected with the time-resolved photoelectron spectroscopy at high pump intensities. While in my visible-pump/EUV-probe scheme I aim for a single-photon electronic excitation of the semiconductor, the large number of photons reaching the surface in a short time interval (about $10^{13}$ in 70 fs corresponding to ~10 GW/cm²) also leads to multiphoton emission (MPE) of energetic electrons, as depicted in Fig. 6.2. In the case of low energetic probe photons in the visible or UV range the strong MPE electron background will obscure the pump-probe photoelectron signal and has therefore restricted such studies in the past to considerably lower intensities. I overcome this
problem by use of EUV probe photons with 70 eV energy and so I achieve sufficient energy separation between the measured signal and the MPE low energetic electron tail becoming confined to energies below 11 eV for 10 GW/cm\(^2\) pump intensity. However, the signal electrons will still be affected owing to vacuum space charge\(^{156}\). 

In the following I will use the maximum kinetic energy - MPE cut-off - of the MPE background electrons rather than pump intensity which depends on the spatial pump pulse profile. The study of the copper valence band photoelectron spectra in the highly excited regime has been selected as an example of a system which does not exhibit the SPV effects and therefore permit an independent study of the vacuum space charge influence on the measured photoelectron spectra without interfering SPV effect. The Cu(100) surface excited with pump pulse of 1.55 eV photon energy producing the MPE background electrons with up to 35 eV kinetic energy has been probed with probe pulse of 70 eV photon energy. The Cu(100) crystal has been cleaned with repeated cycles of Ar\(^+\) sputtering (1.5 keV) and annealing at 580 °C, in the last cycle only at 200 °C to avoid surface contamination from the bulk. The surface cleanliness has been verified by a contamination-free Auger electron spectrum (Appendix B – Fig. B.2). The Cu valence band photoelectron spectra excited with a probe pulse in the presence and absence of pump pulses are shown in Fig. 6.3. I have decided
to use the pump pulse with photon energy of only 1.5 eV to avoid direct photoexcitation from the d-bands\textsuperscript{322} of Cu valence band and so be able to observe a well defined d-bands edge also at high pump intensities. The Cu valence band photoelectron spectra for time delays ±100 fs between pump and probe are identically shifted to higher kinetic energies without significant broadening of spectral features. This can be understood as an acceleration of the leading fast probe photoemitted electrons by Coulomb repulsion from the trailing cloud of slow MPE pump photoemitted electrons. In the following I therefore express the measured SPV transients in terms of a time-dependent relative shift with respect to the situation when the probe pulse precedes the pump pulse by 800 fs (negative delay).

![Fig. 6.4 Photoelectron spectra of the p-GaAs(100) excited with a spectrally pure 45th high harmonic. The inset shows the simplified GaAs electronic structure.](image)

Time-dependent photoinduced changes of the band-bending were studied for p-doped (Zn: 3x10\textsuperscript{19} cm\textsuperscript{-3}) GaAs(100) as well as n-doped (Te: 6x10\textsuperscript{17} cm\textsuperscript{-3}) GaAs(100) surfaces. The clean surfaces were prepared as described in detail in section 4.1. The photoelectron spectrum of the clean p-GaAs(100) surface is shown in logarithmic scale in Fig. 6.4. The photoemission cross section for Ga-3d core-level electrons is nearly two orders of magnitude higher than that for the valence band electrons. This is the reason why the currently feasible short photoelectron accumulation times are prohibiting the direct observation of the electron population dynamics in the conduction band or surface states as a result of insufficient photoelectron signal statistics. Accordingly, in the further text I deal exclusively with the
Ga-3d core-level photoelectrons. The inset of Fig. 6.4 shows also a simplified (without band-bending) electronic structure of the GaAs crystal. The most stunning feature of the photoelectron spectrum in Fig. 6.4 is the absence of the adjacent high harmonics photoelectron signal vanishing in the secondary electron background. This can be achieved by the interplay of the high harmonics driving fundamental wavelength and the incident angles of multilayers. This method is yielding a nearly spectrally clean single high harmonic selection.

Fig. 6.5 Shift of the Ga-3d core-level of (a) p-GaAs and (b) n-GaAs probed 400 fs before and after photoexcitation. The calculated peaks’ center-of-gravity are shown as vertical continuous lines for +400 fs and vertical dashed lines for -400 fs. The insets show schematically the photoinduced band-bendings.
For an energy of 270 µJ/cm² deposited by each 3.1 eV pump pulse neither changes of the Ga-3d core-level spectra by photochemical decomposition nor any macroscopic alterations of the GaAs surface have been observed after the pump-probe experiment with irradiation over several hours. The deposited energy by the pump pulses is lower than the known photochemical decomposition intensity threshold of some 20 mJ/cm² specified for p-GaAs(100) in Ref. 161 or 1 mJ/cm² for n-GaAs(110) in Ref. 155. In Fig. 6.5(a) are presented photoelectron spectra of the Ga-3d inner shell of the p-GaAs(100) at positive and negative pump-probe delay. The observed transient shift of the Ga-3d photoline center-of-gravity towards higher energies after photoexcitation (+400 fs) corresponds to a partial screening of the electric field in the SCR by the mobile carriers created by the optical pump pulse. According to Fig. 6.1 this in turn leads to a reduction of the effective binding energy of the Ga-3d state at the semiconductor surface. Due to the different doping concentrations of n and p-GaAs crystals I am not expecting the same amplitude of the shifts for these two crystals but finding the corresponding shift for n-doped GaAs(100) at lower kinetic energies as indicated in Fig. 6.5(b) I can exclude this effect as being induced by repulsion from MPE electrons as discussed in the case of vacuum space charge. Rather, the opposite sign is compatible with a reduction of band-bending towards higher effective binding energy as expected for n-doping. Since the p-doped crystal exhibited a more pronounced transient energy shift, I focused my investigation on the p-GaAs(100) as indicated in Fig. 6.6 as a sequence of photolines at different visible/EUV time delays. To rule out possible adsorbates induced core-level chemical shifts from residual gases, photochemical decomposition, and temporal drifts of the laser or the electron detection system during the long photoelectron acquisition times the spectra with subsequent time delays have been measured in a random fashion rather than in an ascending order. The pump-probe spatial overlap was verified every time when the time delay has been changed by more than 1 ps with the retractable pinhole of 1.2 mm diameter and a CCD camera. The Fig. 6.6(a) shows the photoelectron yield as a function of time delay and electrons’ kinetic energy. For negative time delays - which corresponds to the situation when probe pulse precedes pump pulse - I observe no significant variations in the Ga-3d photoline. For positive time delay smaller than 1 ps I notice a kinetic energy shift of Ga-3d photoelectrons to higher kinetic energies.

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8 The visual inspection of the used part of GaAs surface in the pump-probe experiment revealed no changes when compared to the unexposed part of surface examined with a light microscope and magnification up to 200x.
Fig. 6.6 Transient in p-GaAs(100) revealed by the Ga-3d core-level shift as a function of the pump-probe delay - (a) contour plot and (b) for selected time delays. The thin vertical lines in graph (b) indicate the peaks’ center-of-gravity positions.
Photoexcitation of the electron-hole pairs in the SCR is followed by the charge separation phase, where the electrons are drifting to surface and the holes into the bulk. This charge transport is connected with gradual decrease of the SCR electric field and corresponding flattening of the electronic bands as well as core-levels. This typical behavior can be seen also in Fig. 6.6(b) for time delays +100 fs and +1 ps. For time delays longer than 1 ps I observe slow gradual decrease of the Ga-3d photoelectrons’ kinetic energy. This phase is linked with the surface recombination processes (see Fig. 6.6(b) for delay times +8 ps, +32 ps). The measured recombination has nearly exponentially decaying character recovering the old value of the band-bending approximately after +32 ps. Fig. 6.6(b) shows also Ga-3d photoline in the absence of pump pulse. Accordingly, I observe a permanent shift with respect to the non-pumped surface as a collective result of the band-bending induced by a possible pre-pulse preceding the femtosecond pump pulse by 12.9 ns, of residual non-decayed carriers from the previous pump pulse 20 ms before and of the vacuum space charge effect as discussed above.

Fig. 6.7 Effect of the vacuum space charge created by pump pulses on the Ga-3d photoelectrons’ kinetic energy at n-GaAs(100) surface
In order to understand the effects of the vacuum space charge created by pump pulses on the Ga-3d photoelectrons I have measured the Ga-3d photoelectrons’ kinetic energy for different pump fluences at n-GaAs(100). The SPV effect on the n-GaAs(100) surface shifts the kinetic energy of the Ga-3d photoelectrons to lower kinetic energies. In Fig. 6.7 Ga-3d photoelectron spectra are shown for three different cases - without pump pulses (Fig. 6.7(a)), at the pump intensities when no vacuum space charge has been generating (Fig. 6.7(b)) and at the pump intensities generating vacuum space charge consisting of the MPE electrons with 11 eV kinetic energy cut-off (Fig. 6.7(c)). In the regime when no vacuum space charge has been generated the SPV effect is dominant and the Ga-3d photopeaks have lower kinetic energy than the Ga-3d photopeak measured at the unpumped surface (Fig. 6.7(b)). In this case the Ga-3d photopeaks 400 fs before and 400 fs after photoexcitation do not differ remarkably in their position. It has been shown\textsuperscript{161} that the ratio of the amplitudes of fast and slow SPV shifts are about 14%. In this case the fast transient SPV shift should be some 60 meV which needs a better photoelectron statistics to prove it. In Fig. 6.7(c) the presence of vacuum space charge built of the electrons with kinetic energy cut-off of 11 eV is shifting the Ga-3d photopeaks to higher kinetic energies. The position of the Ga-3d photopeaks in this case is nearly the same as the position for the unpumped surface which is associated with the generated vacuum space charge and will be different for the vacuum space charge with other electrons’ kinetic energy cut-off. This case clearly demonstrates how vacuum space charge affects the kinetic energy of Ga-3d photoelectrons. In the spectra shown in Fig. 6.7 the shift due to the SPV effect is nearly the same but opposite to that of vacuum space charge. This case also explains the difficulty to obtain the absolute SPV shifts in the presence of vacuum space charge. The Ga-3d photopeaks show also the mentioned fast SPV transient shift observed as a slight shift of the Ga-3d photopeak to lower kinetic energies after photoexcitation (Fig. 6.7(c)).

For completeness Fig. 6.8 shows the measured SPV transient for the n-GaAs(100). The phenomena yielding Ga-3d photopeak shifts in the opposite direction is the same as for p-GaAs(100) only the roles of the electrons and holes are exchanged. After photoexcitation the electrons in the SCR are drifting into the bulk and holes to the surface. This is leading to the flattening of the electronic bands as well as core-levels originally bent upwards. The Ga-3d photoelectron spectra for the positive time delay shorter than 1 ps show shifts to lower kinetic energies. The surface recombination processes tend to restore the original Ga-3d peak position for time delays longer than 1 ps.
Fig. 6.8 Ga-3d core-level peak as a function of the pump-probe delay - (a) contour plot and (b) for selected time delays. The thin vertical lines in graph (b) indicate the peaks’ center-of-gravity positions.
6.2 Dynamics of the band-bending for p-GaAs(100)

An extraction of quantitative values for the SPV changes demands some attention because of overlapping pump and probe beams with the same diameter of approximately 1.2 mm but an inhomogeneous spatial profile as shown simplified in Fig. 6.9. Photoelectrons originating from the less pumped outer region therefore experience a correspondingly smaller SPV shift as compared to the central region of the pump spot and the observed net shift actually represents an integration over the whole area.

Correspondingly, the measured Ga-3d peak profile \( s(E) \) is given as an integral of the unperturbed Ga-3d peak profile for the unpumped surface \( p(E) \) and a weighting function \( g(\Delta E) \) describing the amplitude of the SPV effect as a function of the energy shift which in turn depends on the spatial pump intensity profile \( I(x,y) \)

\[
s(E) = \int_0^{\Delta E_{\text{max}}} g(\xi) p(E - \xi) d\xi \quad (6.1)
\]

where \( \Delta E_{\text{max}} \) is the maximum observed SPV shift. Deconvolution of the photoelectron peak profile \( s(E) \) requires exact knowledge of the spatial profile of the pump beam which has been not recorded. Generally, there are three simple possibilities how to extract data on the
transient SPV shifts observed with my measurements. I restrict the analysis to the extraction of the maximal SPV shift induced with the most intense part of the spatial pump pulse profile. 
i) In a first approximation I can fit my data with two peaks, where one is fixed and the second one is moving. Each of the peaks is a replica of the Ga-3d peak in the unpumped condition. This method is quite good but it can not always fit properly the profile of the measured Ga-3d peak. ii) Second possibility is to concentrate the attention only to the highest energetic edge of the Ga-3d peak profile. In this case I can use a second derivative to find the inflexion point which is tracking very precisely the maximum Ga-3d kinetic energy shift. However this method is very sensitive to the peak profile and very good photoelectrons’ peak statistics is required. iii) The last method is the center-of-gravity determination. This very robust method has limited sensitivity for the subtle changes at the highest energy edge of the Ga-3d peak because of the not weighting nature of the center-of-gravity calculation. Although reduced sensitivity for the fine changes at the highest energy edge of the Ga-3d photopeak I use this method as primer source of the information on the observed band-bending dynamical processes. The center-of-gravity $E_C$ and its standard deviation (shown as error bars) $\Delta E_C$ has been calculated as follows$^{369}$

$$E_C = \frac{1}{\sum E N_E} \sum E \cdot N_E$$

$$\Delta E_C = \frac{1}{\sum E N_E} \sqrt{\sum E (E - E_C)^2 \cdot N_E}$$

where $N_E$ denotes the number of photoelectrons with kinetic energy $E$ and summation in $E$ runs over the region of interest. In the derivation of equation (6.3) the Poisson probability distribution of the registered photoelectrons has been utilized.

In Fig. 6.10 the transient shift of the Ga-3d photopeak is shown as a function of the time delay between pump and probe determined with the center-of-gravity calculation. The reliability of the center-of-gravity shifts has been verified by repetitive measurement of the shift for +1 ps time delay one hour later under the same experimental conditions. These measured shifts are shown inside of the gray bar in Fig. 6.10(b). The calculated error bars in Fig. 6.10 with equation (6.3) are showing the Gaussian standard error interval$^{361}$ 1σ corresponding to 68.3% of all measured shifts.
Fig. 6.10 Temporal evolution of the Ga-3d peak’s center-of-gravity in linear (a) and semi-logarithmic (b) time scale after photoexcitation of the p-GaAs(100) surface.
However the shift for +1 ps time delay measured one hour later does not fall in the standard 1σ confidence interval and only the confidence interval based on 2σ corresponding to 95% of all measured shifts can justify the shift measured one hour later. A different value of the observed shift points to possible deterioration of the surface conditions. To solve this problem I have to achieve better vacuum of order 1x10^{-11} mbar. The pointing laser stability resulting in the falling conversion efficiency for high harmonics (Fig. 3.9) and in the changes of the spatial pump profile are also an error source contributing to the measured different values for the SPV shifts. In order to reproduce the measured SPV shifts one needs the precisely same prepared and reconstructed surface. Already small differences in the surface preparation are yielding different SPV transients as shown in Appendix C. The temporal coincidence of pump and probe pulses found with the interferometric method is precise within 100 fs due to small required re-adjustments needed afterwards. Daily operation and measurements on highly photoexcited n-GaAs(100) has proved a sudden shift of the Ga-3d peak at +100 fs. On this basis I believe to find the pump-probe temporal coincidence in Fig. 6.10 at about +100 fs. In Fig. 6.10 there are noticeable Ga-3d peak shifts for negative time delays. The reason for the observed phenomenon could be found in the temporal pump pulse profile. The highly dynamic autocorrelation measurements characterizing femtosecond pulses from CPA laser systems\(^{365}\) show that the light intensity at 1 ps before the pulse arrival is some 10^-6 of the maximum intensity and at a few hundreds femtosecond some 10^-3 of the maximum intensity. Since the SPV effect is not linear\(^{136}\) with the pump intensity, at high pump fluences as used in this study it tends to saturate. It is quite possible that already few hundreds femtoseconds before the pump pulse arrival the intensities of some 10^-3 of the pump pulse intensity are contributing to the observed slight Ga-3d photopeak shifts. The Ga-3d shifts shown in Fig. 6.10 are relative to the negative time delay at -800 fs. Fast carrier transport in the photoexcited semiconductor bulk to the probed surface through an acceleration in the strong SCR electric field manifests itself in a reduction of band-bending and a corresponding peak shift within less then 500 fs after the pump pulse. The subsequent carrier relaxation by recombination and trapping in surface states is observed to occur on a slower time scale\(^{148,151}\) of a few picoseconds. The dynamical behavior in Fig. 6.10 can be well fitted with a convolution of an exponential decay and a gaussian function of the form

\[
e^{-\frac{t}{\tau}} \left[1 + \text{erf} \left( \frac{t - \frac{w}{2\tau}}{\frac{w}{2\tau}} \right) \right]
\]  

(6.4)
where $\text{erf}$ is the error function\(^8\). The fitting procedure based on the method of least squares is yielding the mean values and their standard deviations of $w = 600 \pm 180 \text{ fs}$ for the rise time and $T = 15 \pm 3 \text{ ps}$ for the decay time. Electrons transit times of about 500 fs in p-GaAs were predicted by simple theoretical considerations\(^{139,145}\), assuming solely the electron drift with the saturation velocity through the SCR, albeit for lower doping of $10^{18} \text{ cm}^{-3}$ with a correspondingly larger SCR. An extraction of more detailed information on the carrier dynamics for the studied system will be obtained by solving the complex set of coupled differential equations (2.19)-(2.21) connecting electron-hole creation, charge transport, relaxation and modification of the electric field in the SCR by the transient charge redistribution. For completeness the transient Ga-3d peak shifts for the n-GaAs(100) with significantly lower dopant level is shown in Fig. 6.11. The observed Ga-3d peak shifts to lower kinetic energies as has been expected. Surprisingly, the Ga-3d shift occurs within 400 fs which is faster than for the p-GaAs surface. At this stage I need support by a theoretical simulation to interpret the measured results.

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \]

---

Fig. 6.11 Temporal evolution of the Ga-3d peak’s center-of-gravity after photoexcitation of the n-GaAs(100) surface.
Chapter 7

Conclusions and Outlook

In the framework of this thesis novel apparatus for the femtosecond time-resolved photoelectron spectroscopy in the EUV region has been built. The CPA femtosecond laser system based on regenerative and multipass amplification has been constructed and characterised. By focusing the laser beam in the pulsed Ne gas jet the high harmonic has been generated. The key position in the experimental apparatus is the low group velocity dispersion EUV monochromator\textsuperscript{46} selecting single high harmonic without its temporal distortion. The specially tailored multilayer low gamma Mo/Si mirrors\textsuperscript{47} has been applied for the selection and reflection of single high harmonic. Using the TOF electron spectroscopy and selected high harmonic the first static photoelectron spectroscopy on the rare gases has been performed\textsuperscript{45}. The excellent spectral selectivity of the EUV monochromator has been investigated via photoelectron spectroscopy of He gas. The UHV compatibility of this apparatus made the photoelectron spectroscopy of the solid states surfaces also possible. The first photoelectron and Auger electron spectra of the Pt(110) surface as well as Ga and As core-levels by the photoemission from GaAs(100) surface has been observed. The chemical shift of the W 4f core-levels has been studied on W(110) crystal surface and W(CO)$_6$ adsorbate. The iodine films 4d core-levels and valence band photoemission together with Auger electron spectra has been observed. Also the Ga-3d core-levels and valence band photoelectron spectra of a complex organic molecule Ga$_3$q has been investigated. The visible-pump/EUV-probe technique has been implemented for the observation of the ultrafast hot electron relaxation on
a Pt(110) surface\textsuperscript{48}. The valence band electron dynamics of highly excited Pt surface has been observed. The valence band depopulation effect due to the total excitation of 2.2\% of all valence band electrons has been examined. The following cooling of hot electrons accompanied by the rise of crystal lattice temperate has been analysed. Due to short lifetime of hot electrons of a few femtoseconds a visible-pump/EUV-probe cross-correlation has been measured and constitutes the first UHV compatible technique for the measurement of femtosecond high harmonic duration. The principle is based on the short living hot electrons excited into the unoccupied states above the Fermi level and emitted with the time-delayed high harmonic probe pulse. The visible-pump/EUV-probe time-resolved core-level photoelectron spectroscopy has been utilized for tracking the charge carrier dynamics on semiconductor surfaces. Transient changes of the surface photovoltage at the p-GaAs(100) surface has been observed after photoexcitation with femtosecond pump pulses. The time evolution of the band-bending has been probed by measuring the kinetic energy shifts of the Ga-3d core-level photoelectrons after excitation with femtosecond EUV probe pulses. Carrier transport from the bulk to the surface has been observed to occur within 500 fs after photoexcitation while a subsequent relaxation has been determined to evolve on a time scale of a few tens of picoseconds.

I hope that in this thesis I have convinced about usefulness, capability and great potentials to address core-level electrons by the femtosecond time-resolved photoelectron spectroscopy in the EUV region. An application of this experimental technique for the observation of electron dynamics at high pump intensities on semiconductors surfaces\textsuperscript{366} and the dynamics of chemical bonding of ordered organic layers on surfaces\textsuperscript{367} will give new physical insights on these two promising branches of the ultrafast processes. It makes me believe that my core-level based time-resolved experiment is predetermined to offer a deeper view on highly photoexcited semiconductors surfaces not accessible with other time-resolved techniques. The traditional time-resolved studies of the chemical bonds are based on the changes induced in the bonding molecular orbitals. However, the complex organic molecules consisting of large number of elements have the valence band structure which changes are not easy to interpret and locate one particular site in the molecule where the chemical bond had changed. The idea of “marker atom” embedded in the site of interest and application of time-resolved photoelectron spectroscopy on the core-level electrons of this particular “marker atom” will provide the information on the dynamics of complex molecular systems in the very proximity of the “marker atom“ rather than on the “site-unspecific” changes of the valence band.
Appendix

A Knife-edge Beam Profile Measurement

The most simple technique of the EUV beam profile analysis is so-called knife-edge technique. The EUV beam before the TOF electron spectrometer has been gradually blocked by the knife-edge plate and the passing residual light has been measured with the MSP intensified photocathode (see Fig. 3.1). The measured signal proportional to the EUV intensity as a function of the knife-edge position is shown in Fig. A.1. On the assumption that EUV beam has spatially homogenous Gaussian profile\textsuperscript{368} the measured data can be fitted with a function

\[ I(x) = \frac{I_0 w \sqrt{\pi}}{2 \sqrt{2}} \int_{-\infty}^{\infty} e^{-r^2} dt \]  

where \( I_0 \) is the maximum of light intensity and \( 2w \) is the full width at e\(^{-2}\) of \( I_0 \). Under these conditions the fitted beamwidth is \( 2w = 1.2 \) mm.

Fig. A.1 The measured EUV light intensity as a function of the knife-edge position. The grey curve shows the corresponding fit on the assumption of the Gaussian beam profile.
Appendix

B Auger Electron Spectroscopy on Pt, Cu and GaAs Surfaces

The Auger electron spectroscopy\textsuperscript{287} (AES) has been used to check on the quality of surface cleanliness. The excitation electron beam with the kinetic energy of 1.25 keV has been impinging under 75° to the surface normal. The AES spectra has been collected with self-made retarding field analyser\textsuperscript{369}.  

![Fig. B.1 The AES spectra of Pt(110) surface before (a) and after (b) cleaning procedure. Thin vertical lines indicate the characteristic electron peaks of platinum and carbon.](image)

The AES spectra of Pt(110) surface before and after cleaning are shown in Fig. B.1. The initial carbon contamination has been removed during the cleaning procedure. In Fig. B.2 are shown the AES spectra of Cu(100) surface before and after cleaning. In the region between 100 eV and 600 eV there are no characteristic lines of copper and only the main contaminants like sulphur and carbon are visible. These were eliminated during the cleaning procedure. The Fig. B.3 shows the AES spectra of GaAs(100) surface. Again in the measured region between 100 eV and 600 eV there are neither the characteristic lines of gallium nor arsenic. The carbon
contaminants as well as native gallium and arsenic oxides were removed during the cleaning procedure.

Fig. B.2 The AES spectra of Cu(100) before (a) and after (b) cleaning procedure. The vertical lines show the position of electron peaks of carbon and sulphur contaminants.

Fig. B.3 The AES spectra of GaAs(100) before (a) and after (b) cleaning procedure. The contamination due to carbon and native oxides show the vertical lines in the electron spectra.
Appendix

C Surface Photovoltage Transients and Surface Preparation

The SPV transients are highly sensitive probe of the semiconductor surface conditions. This is demonstrated in Fig. C.1-C.3. The p-GaAs(100) and n-GaAs(100) surfaces has been prepared as described in section 4.1. Although the preparation conditions varied only in a few minutes in the duration of the sputtering and annealing times the behaviour of the SPV transients were radically influenced. This is shown for p-GaAs(100) in Fig. C.1-C.2 (compare with Fig. 6.10). This has been also observed for n-GaAs(100) in Fig. C.3 (compare with Fig. 6.11).

Fig. C.1 Temporal evolution of the Ga-3d peak’s center-of-gravity after photoexcitation of the p-GaAs(100) surface.
Fig. C.2 Temporal evolution of the Ga-3d peak’s center-of-gravity after photoexcitation of the p-GaAs(100) surface.

Fig. C.3 Temporal evolution of the Ga-3d peak’s center-of-gravity after photoexcitation of the n-GaAs(100) surface.
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