6 Summary and Outlook

This work presents time-resolved photoemission measurements where femtosecond laser and synchrotron radiation was combined in a pump-probe setup. The main subject is to developed and test the experimental method used in this work, which is an intermediate step between conventional 2PPE laser-pump laser-probe experiments, where only optical energies are reached and the now emerging field of high harmonic generation (HHG) where soft X-rays become available.

6.1 Vanadium Dioxide

The photoemission study of vanadium dioxide (VO_2) intended to give a complete characterization of the temperature induced metal to semiconductor phase transition. Two different growth techniques of VO_2 films have been described with film thickness ranging from a few monolayer to 200 nm. In addition different substrates have been tested to study the film-substrate interface and its influence on the phase transition. Results are summarized in Table 6.1. Finally, the study aimed at inducing phase transition in VO_2 by laser excitation.

For all epitaxial films grows on a TiO_2 substrate it was impossible to determinate a

	Relative shift of V 3d edge [meV]	Transition Temperature [K]
< 8 ML VO_2 on TiO_2 ultrathin film	33	*no*
100 nm VO_2 on TiO_2 thin films	48	*no*
VO_2 on SiO_2 1 time annealing	100	300
VO_2 on SiO_2 3 times annealing	97	220

Table 6.1: Comparative study of VO_2 films of different thickness and on different substrates.

well-defined transition temperature. The changes of the vanadium 3d valence-band edge are not very significant.

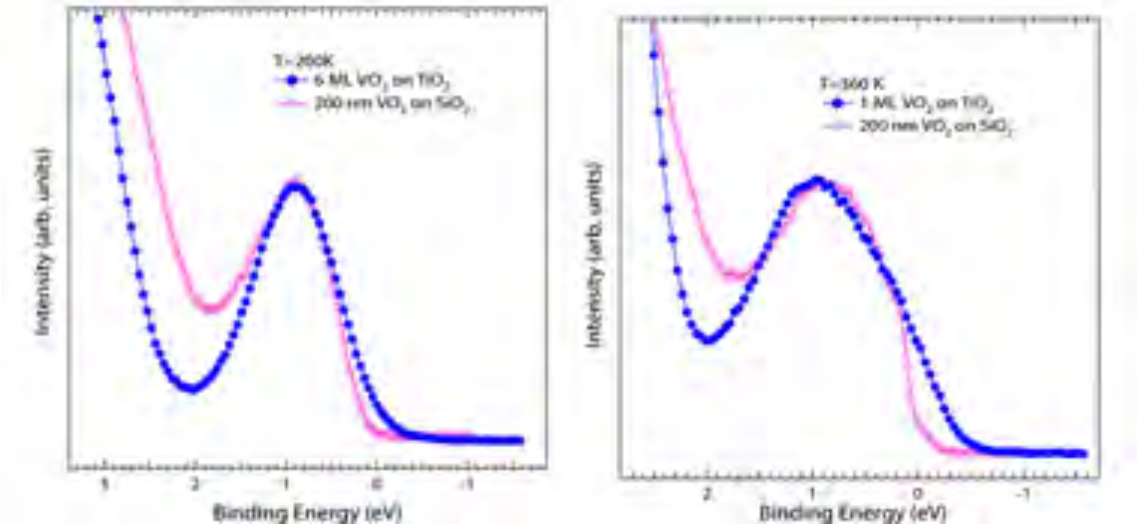

Figure 6.1: Valence-band spectra of VO_2 films on TiO_2 and on glass. a) for temperatures below 200 K. b) For temperatures above 360K K. The semiconductor to metal phase transition is only evident for the 200 nm thick VO_2

We conclude the phase-transition is suppressed by strong interaction between the substrate and the epitaxial film.

To avoid this interaction at the interface between substrate and films were prepared by radio-frequency sputter-deposition 200 nm thick VO_2 films on silica. The films exhibit a significant shift of the V 3d valence-band edge and a change of the shape of the V 3d spectral region as a function of temperature. The films do not show a single-crystalline structure, but, nevertheless, a clear transition temperature point can defined. An important finding is that the transition temperature for these amorphous films is lower than reported in previous studies [Mor59].

Figure 6.1 shows a comparison of valence-band spectra to epitaxial grown and RF sputtered films. At lower temperatures only the RF sputtered film exhibits semiconducting behavior (Fig. 6.1a). These films become metallic above 300 K (Fig. 6.1b). Upon laser excitation heat accumulation made a study of the dynamics of the phase transition impossible. The phase transition occurs due to an increase of the temperature of the sample and is not photo-induced by the femtosecond laser pulse as would have been desirable.

The most important finding is the dependence of the phase transition on sample treatment. After repeated annealing the phase-transition temperature increases likely due to a creation of defects or oxygen vacancy.

Moreover, the nature of the phase transition changes from Metal-to-Semiconductor

for the first preparation to Semiconductor-to-Semiconductor transition for further preparation cycles.

6.2 The Clean Si(100)-c(4x2) Surface

The time-resolved measurements on Si(100)c(4×2) are the main part of the present thesis. They have been performed using the low-α operation-mode of the BESSY storage ring, where synchrotron bunches deliver probe pulses of about 10 ps duration. They set the time-resolution and thereby demonstrate the quality of the synchronization.
The bulk plasma-density induced by infrared laser excitation of 110 mJ/cm^2 is about 10^{21} carriers/cm^3. This value is deduced from the observed band-gap narrowing of 220 meV and corroborated by calculations. The relaxation of the carriers can be described by Auger decay with a decay constant of C_{e-h}=6.4·10^{-33} cm^6/s. Excited bulk carriers live for several tenths of picoseconds.
We observe transient changes of the electronic structure of Si(100) and they can be clearly separated from space charge effect and surface photovoltage.
The pump-pulse with a photon energy of 1.56 eV leads likewise to population and depopulation of the unoccupied and occupied surface bands D_{down} and D_{up}. The relaxation of the excited electron and holes in the dangling-bond bands is governed by two contributions. A linear term describes the scattering into defects or bulk states, while a quadratic term quantifies the surface recombination of excited electron-holes pairs. Decay parameters obtained are in agreement with the values of Bokor [Hal89].

Si 2p core-level spectra have been measured for laser excitations with a fluence of 40 mJ/cm^2. The Si 2p spectra were deconvoluted in seven double Gaussian functions, to distinguished surface from bulk components. The laser pump-pulse induces changes of the surface component but leaves the bulk component almost unaffected. This broadening of the surface component of the Si 2p core-level is attributed to a variation of the dimer buckling angle upon charge redistribution at the surface. For 40 mJ/cm^2 laser excitation the carrier excited concentration at the surface is approximately 10^{14} cm^2. DFT calculations show that this carrier redistribution induces a softening of the dimer potential with respect to the buckling angle. In consequence a new transient structure is stabilized for about 100 picoseconds.

6.2.1 Outlook

Near X-rays absorption fine structure (NEXAFS)spectra have been recorded at undulator U125/1 PGM for Si(100) with the analyzer turned to a kinetic energy of 80 eV. Two resonances at approx. 0.8 eV and 1.35 eV below the $L_{II,III}$ absorption

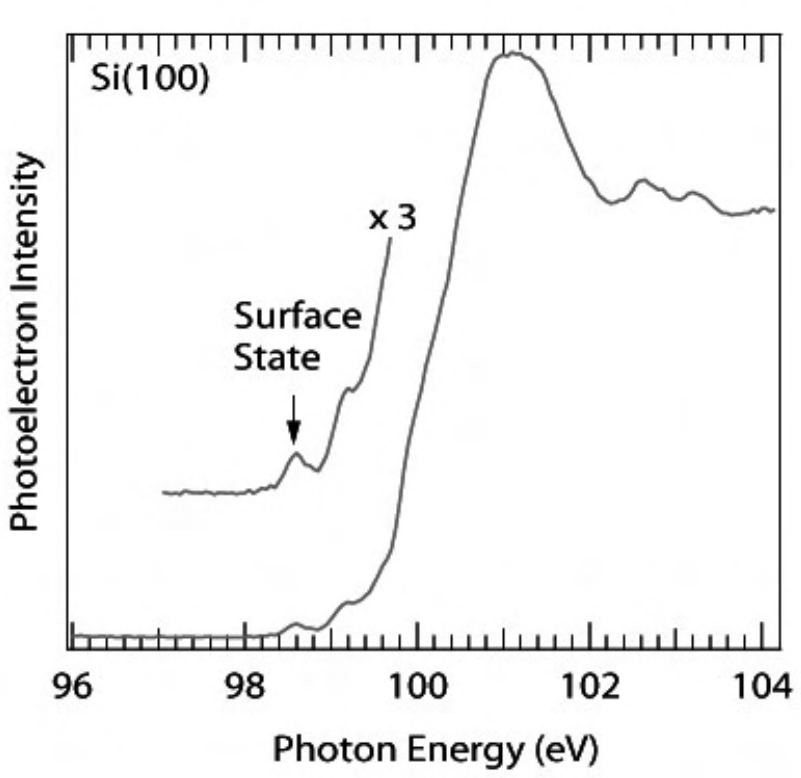

Figure 6.2: Silicon $L_{II,III}$ absorption edge. The surface state is easily distinguished from bulk states. The kinetic energy was fixed at 80 eV and the photon energy was tuned from 96 to 110 eV.

edge are observed. They are attributed to transitions from the Si $2p_{3/2}$ and Si $2p_{1/2}$ core-level to the unoccupied dangling-bond band. Probing these states via NEXAFS allows to separate surface from bulk states. Therefore, time-resolved measurements at the $L_{II,III}$ absorption edge could help to better understand electron dynamics.

6.3 Magnetization Dynamics in Gd(0001)/W(110)

The time-resolved photoemission spectroscopy at Gd of the 4f core-level of Gd(0001) for 100 Å thick films on W(110) have been performed in singlebunch operation mode at the undulator beamline U125/1 PGM of BESSY. The pump-laser used was an infrared laser with 100 fs pulse duration with the absorbed laser fluence is about 3.5 mJ/cm^2.
The aim of this pump-probe experiment was a direct measure of the temporal evolution of the 4f core shell contribution to the magnetization. After excitation with an ultrashort laser pulse the transient magnetization is monitored by linear dichroism of the Gd 4f photoemission spectra.

Three effects happen upon laser excitation: the spectra shift to higher kinetic energy, they broaden slightly and the overall dichroic signal decreases. The temporal evolution of the shift and broadening differs from the temporal evolution of the decrease of the dichroic signal. The drop of magnetization is about 20 % upon laser excitation. The magnetization and thus the dichroic signal remain unchanged at negative pump-probe delay. The magnetization recovers in about 250 ps. This time scale is consistent with a magneto-optical experiment and is attributed to heat diffusion after laser excitation. Fig. 6.3 sketch the really separation between excited valence electrons, phonons and 4f spins system. The duration of the synchrotron electron-bunches of 40-80 ps in single bunch operation does not allow to clarify the dynamics of ultrafast demagnetization. Nevertheless, it is demonstrated for the first time that following the dynamics of the Gd 4f core-level is a new pathway to study the magnetization dynamics in gadolinium. Indeed, time-resolved core-level photoemission spectroscopy is useful method to investigate ultrafast demagnetization once femtosecond soft X-ray sources become available. The evolution of XUV femtosecond laser sources in the near future will not only facilitate time-resolved core-level photoemission spectroscopy, they will also enable an investigation of the Gd(0001) surface to understand the interaction of 5d-4f magnetic moments.

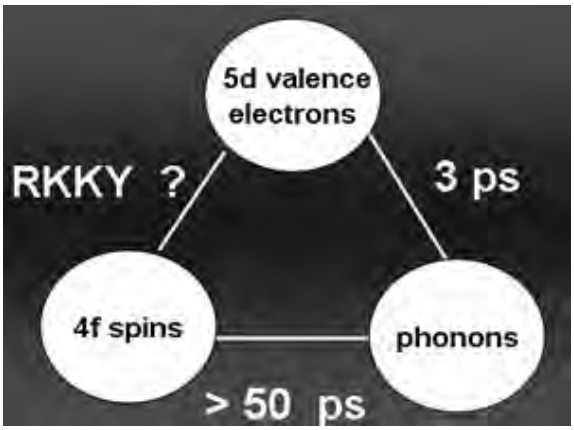

Figure 6.3: The energy flow between various interacting heat baths in Gd for an absorbed pump fluence of 3.5 mJ/cm^2