Introduction

Ultrafast laser ablation technique is currently attracting great attention both for fundamental physics and technological applications. On the one hand, high-powered lasers producing single pulses with output powers in the petawatt region are currently being developed for a whole host of fundamental applications ranging from fusion ignition systems and high-energy particle physics [1] to medical applications involving radioactive isotope generation [2]. On the other hand, the recent advances in ultrafast laser technology have opened up the possibility to use compact ultrafast tabletop laser sources combining multi-MW peak pulse powers and multi-MHz repetition rates for various applications [3].

The first investigations on the interaction of femtosecond laser radiation with solid targets were mainly devoted to the study of modifications of the irradiated samples [4, 5]. These studies are still establishing ultrafast laser ablation as the state-of-art technique for precise control of material removal, due to its ability to process virtually any material with high precision and minimal collateral damage. In a wide variety of applications including cutting, drilling, 3D-micromachining, and surgical operations advantages over nanosecond and picosecond laser radiation have been already demonstrated.

A key benefit of ultrafast laser radiation consists in its ability to deposit energy into a material in a very short time period, before thermal diffusion can take place. Following linear or multiphoton absorption of the laser energy, electron temperatures can quickly rise up to many thousands of Kelvin. With the subsequent energy transfer from the electron subsystem to the atomic lattice, material removal, ablation and plasma formation occur. At laser pulse durations shorter than the typical electron to lattice relaxation times (about some ps), the system's behavior and the main properties of the plume are quite independent from material and laser parameters. On the contrary, for nanosecond laser radiation ablation occurs both in the melted and the vapor phases, leading also to emission of particulates, micro-droplets, and liquid jets. Moreover, the long lasting material emission and the larger pulse duration lead to laser-vapor interaction, limiting the control on the properties of the ablated particles.

Recent experimental studies on large-fluence ablation using ultrafast laser radiation [6], however, indicate that, contrary to theoretical predictions of ultrafast melting and ablation rates, a significant increase in the overall ablation rate and the recast layer thickness can be observed *ex situ*, which causes me-

chanical stress, deformation, and crack formation in material. In addition, experimental observations reveal thermal and non-thermal melting, generation of highly pressurized material vapor, ejection of melt droplets and liquid jets, hundreds of nanoseconds after irradiation [7].

This thesis deals with some important aspects of the interaction of intense femtosecond laser pulses ($I \lesssim 10^{15}$ W·cm^{-2}) with metals and transparent materials. In spite of its enormous potentiality, there has been little work on the characterization of laser produced plasma and plume evolution as well as on melt dynamics using ultrafast laser radiation at these intensities. Since there is still a lack of experimental data for the melt dynamics, an unanimously accepted large-fluence model for prediction of the ejected melt rate, size or velocity does not exist as well. Thus, one of the main goals of the present thesis is to elucidate some of the fundamental aspects regarding the laser-matter interaction, plasma formation, evaporation, melt expulsion, and its dynamics (Figure 1). Due to the different time scales of these phenomena, the development and application of novel experimental techniques as well as the systematic analysis of the observed dynamics have been matter of research.

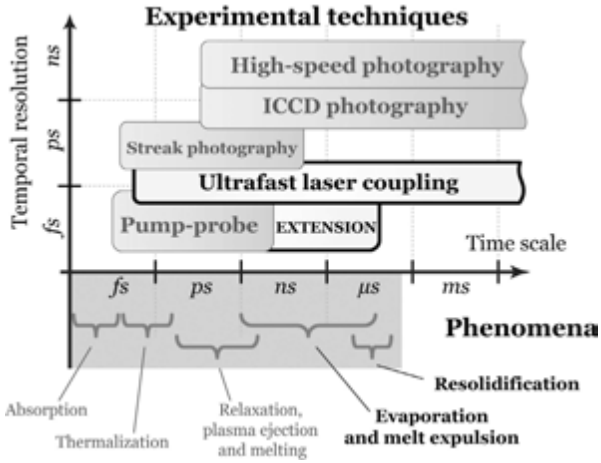

Figure 1: Map of phenomena during ablation of materials with ultrafast laser radiation and experimental techniques for its detection.

Investigations of the ultrafast melting of matter is the main goal of this thesis. On the one hand, melting and accompanying ablation of metals irradiated by single ultra-short laser pulses at large intensities ($I \approx 10^{12} - 10^{15}$ W·cm^{-2}) is investigated. On the other hand, another approach for the ultrafast melting, particularly in the volume of transparent dielectrics is studied by utilizing high-repetition rate ($f_{rep} = 0.1 - 5$ MHz) laser radiation

including heat accumulation effects.

Pump-probe imaging techniques have been adopted for the investigation of laser-induced phenomena, such as vaporization and melt expulsion. In order to enable time-resolved measurements on large time scales up to $\tau \approx 2$ μs preserving ultra-short temporal resolution ($\Delta t \approx 100$ fs), an extended multi-pass delay stage has been designed and applied.

For the detection of laser-induced optical phase changes during laser-matter interaction, a new concept has been developed – called Transient Quantitative Phase microscopy (TQPm). This new non-interferometric pump-probe visualization technique enables time-resolved quantitative measurements of optical phase changes in order to determine object's properties, e.g. dimensions of melt droplets and layer thickness or transient refractive index changes in transparent materials. A calibration procedure for compensation of misalignments and intensity deviations has been developed and adopted.

In this work, ablation of pure metals (Au, Al, Cu, Fe, W) irradiated with femtosecond laser radiation ($t_p = 80$ fs) at large intensities ($I \leq 4{\cdot}10^{15}$ W$\cdot$cm^{-2}) has been investigated *in situ* using time-resolved shadowgraphy and TQPm [8]. Time-resolved quantitative measurements of the ablated volume of material have been performed up to the delay $\tau = 1.81$ μs after irradiation utilizing a pump-probe technique.

For a commercial femtosecond laser system, the effect of the background radiation pedestals on the ablation has been estimated by measuring intensity and duration of background radiation. Using numerical modeling, the temperature rise induced by the background radiation pedestals has been calculated for different metals, which enables an estimation of pre-heating effects on irradiated material.

Laser ablation of metals has been studied *ex situ* by means of scanning electron microscopy (SEM) and white-light interferometry (WLI) varying the number of incident laser pulses (n = 1..8) and their pulse energies.

Melting of borosilicate glass using high-repetition rate ultrafast laser radiation ($t_p = 450$ fs, $f_{rep} = 0.1 - 5$ MHz) has been studied *in situ* by means of TQPm. By tightly focusing ultrafast laser radiation into the volume of glass, a train of femtosecond laser pulses serves as a point source of heat located inside the bulk, leading to localized melting. This and related phenomena as well as applications in direct micro-welding of glasses are discussed.

This thesis is organized as follows. A compact literature overview about ablation and micromachining of various materials using ultrafast laser radiation is presented in chapter 1. A general overview of the theoretical background is reported in chapter 2, while chapter 3 is dedicated to the description of the experimental apparatus and techniques. Chapters 4 and 5 are devoted to the presentation of the main experimental and numerical results for metals and glasses, respectively.

1. State of the art and research objectives

The study of the laser-material interaction using ultrafast laser radiation is an active area of research. Topics such as the mechanisms of free carrier generation, the transfer of energy from free carriers to the lattice, and the ablation mechanisms for various materials have been matter of research. Investigations of the quality of the ablated area (surface roughness, chemical composition, surrounding damage, etc.) for various materials have also been undertaken. This chapter will provide an overview of the studies of material surface melting by ultrafast laser radiation and micromachining at large irradiation fluences $F \gg F_{thr}$ that have focused on various materials, such as metals, semiconductors and dielectrics. Additionally, investigations of melting in the volume of transparent dielectrics using high-repetition rate ultrafast laser radiation at moderate irradiation intensities are presented in this chapter. A short overview of reported numerical simulations and modeling of melting and ablation mechanisms is also introduced.

1.1. Melting of matter by ultrafast laser radiation

Melting of metals and semiconductors

The interaction of ultrafast laser radiation with semiconductors has been studied time-resolved by a variety of techniques, including time-resolved reflectivity and photoluminescence [9], surface ellipsometry [10], and surface second-harmonic generation [11, 12]. The reflectivity dynamics of bulk silicon irradiated at $\lambda = 620$ nm, $t_p = 80$ fs has been detected from $\tau = 100$ fs to $\tau = 600$ ps after irradiation. A rapid increase in surface reflectivity caused by thermal melting occurs. Melting, boiling, and material ejection over a 600 ps period has been detected. The results suggest that, for excitation fluences several times the melting threshold, silicon is ejected from the melted surface as liquid droplets with sub-micrometer dimensions.

Using time-of-flight mass spectroscopy and time-resolved interferometry, melting and ablation of various semiconductors irradiated by femtosecond laser radiation ($\lambda = 620$ nm, $t_p = 100$ fs) has been investigated [13, 14].

Close to the ablation threshold fluences, a maximum surface temperature is obtained from the collisionless time-of-flight distributions of evaporated or sublimated particles. At the melting threshold fluence, the surface temperature for silicon is estimated to approximately 500 K higher than the equilibrium melting temperature. In the fluence regime where non-thermal melting occurs, maximum surface temperatures in excess of 2500 K for silicon and gallium arsenide have been measured, indicating rapid thermalization after the melting. An evidence for an electronically induced amorphous-to-crystalline phase transition in GeSb has been presented [15].

Formation of nanojets and microbubbles on metallic surfaces has been studied by single-pulse irradiation of thin gold films (thickness $d = 60 - 500$ nm) using tightly focused femtosecond laser radiation ($\lambda = 800$ nm, $t_p = 100$ fs, $F \leqslant 3.34$ J·cm^{-2}) [16]. Nanostructures are formed due to hydrodynamic motion of the produced melt when the entire film thickness is locally molten.

The characteristic time for melting of gold nanorods and generation of nanoparticles by ultrafast laser radiation ($\lambda = 400$, 800 nm, $t_p = 100$ fs) has been measured using time-resolved transient absorption spectroscopy [17]. For photo-induced transformation of nanorods to nanospheres, the transformation time has been determined in the range $\tau = 30 - 35$ ps, which is independent of the irradiation power. Furthermore, no significant dependence of the photoisomerization dynamics on the gold nanorod aspect ratio could be detected.

Electrical and thermal properties of bulk copper have been studied on a picosecond time scale using $t_p = 100$ fs laser pulse at large intensity $I \sim 10^{15}$ W·cm^{-2} [18]. Energy dissipation mechanisms and scaling laws spanning a wide temperature range are obtained from femtosecond pump-probe reflectivity measurements. The disassembly of the crystalline structure in copper is observed within $\tau = 400$ fs due to lattice disorder caused by the intense irradiation. The electrical resistivity is detected by studying the temporal development of the reflectivity up to $\tau = 30$ ps after irradiation. A "resistivity saturation" effect has been observed in the phase regime intermediate to plasma and solid state.

A study of the temporal behavior of the optical properties i.e. dielectric function of gold under ultrafast laser excitation ($\lambda = 400$ nm, $t_p = 150$ fs) has been performed by pump-probe diagnostics including reflectivity, transmissivity, and phase shift up to $\tau = 40$ ps after irradiation [19]. Gold films (thickness $d = 25 - 30$ nm) undergo non-equilibrium melting and liquid-plasma transitions over a wide range of irradiation fluences. The results confirm the quasi-stability of the liquid phase that follows non-thermal melting. Disassembly of the liquid into a plasma phase is found to occur at a lattice energy density of $\epsilon = 3.3 \cdot 10^5$ J/kg independent of the irradiation fluence

and ambient pressure.

Femtosecond time-resolved microscopy has been used to analyze the structural transformation dynamics in single-crystalline 100-germanium wafers (melting, ablation, and resolidification phenomena) induced by ultrafast laser radiation ($\lambda = 800$ nm, $t_p = 130$ fs) on a time scale $\tau \leqslant 10$ ns [20]. Complementary information on larger time scales $\tau = 350\,\text{ps} - 1.4\ \mu\text{s}$ has been obtained by means of simultaneous streak camera and photodiode measurements of the sample surface reflectivity. Time-resolved microscopy enables the detection of additional reflectivity patterns for fluences below the ablation threshold fluence of germanium. The observed patterns are originating from the selective removal of the native oxide layer at the wafer surface within a certain fluence range. After resolidification, and in contrast to the ultrafast laser irradiation of other semiconductors, no indication for a laser-induced permanent surface amorphization has been detected. From this observation and the observed transient solidification behavior of the molten germanium on a time scale of some nanoseconds, a lower limit for the critical speed of the liquid/solid interface between $v = 2.5$ m/s and $v = 7.0$ m/s has been deduced.

The study of laser-induced ($\lambda = 800$ nm, $t_p = 40$ fs) solid-to-liquid phase transitions in aluminum has been performed using UV-VIS-IR reflectometry [21]. The transition time scale has been determined to $\tau = 1.5 - 2$ ps, indicating that the transition is thermal, in agreement with electron-diffraction studies [22] adopting electron pulses ($t_p = 600$ fs). The maximum in the reflectivity of solid aluminum at $\lambda = 800$ nm disappears in the liquid state, demonstrating that the parallel band structure typical for solid aluminum is no longer present. The reflectivity of the liquid is smaller than that of the solid and remains constant up to $\tau = 10$ ps, without plasma contributions.

Melting and welding of dielectrics

Using tightly focused ultrafast laser radiation ($\lambda = 800$ nm, $t_p = 100$ fs, $E_p = 5$ nJ), optical breakdown and structural changes in bulk transparent materials have been investigated [23]. Measurements of the threshold fluence for structural change in Corning 0211 glass as well as a study of the morphology of the structures produced by single and multiple laser pulse irradiation have been performed. At a large repetition rate, multiple pulses produce a structural change dominated by cumulative heating and melting of the material by successive laser pulses. Using this effect, optical waveguides have been produced inside bulk glass [24].

The interaction of intense ultrafast laser radiation ($\lambda = 800$ nm, $f_{rep} = 1$ kHz, $t_p = 50$ fs and 200 fs) with wide band-gap fused silica and $\alpha-$quartz has been investigated [25]. During multi-shot target irradiation, melting of SiO_2 occurs. The incubation effect in fused silica leads to high-temperature

and high-pressure conditions that principally favor the phase transition (crystallization) of amorphous fused silica to crystalline quartz.

The formation mechanism of melt rims created by ultrafast laser radiation ($\lambda = 780$ nm, $t_p = 100-200$ fs) on borosilicate glass surfaces has been studied [26]. A thin melt rim is formed around the smooth craters and its height is raised above the undamaged surface by about $50 - 100$ nm. To investigate the mechanism of rim formation following irradiation by a single ultrafast laser pulse, a one-dimensional theoretical analysis of the thermal and fluid processes involved in the ablation process has been performed. The results indicate the existence of a very thin melted zone close to the surface and suggest that the rim is formed by the large pressure plasma producing a pressure-driven fluid motion of the molten material outwards from the center of the crater. A tall rim can be formed during the initial stages of the plasma and tilt towards the low pressure region creating a resolidified melt splash as observed in the experiments.

Focused ultrafast laser radiation ($\lambda = 800$ nm, $t_p = 100$ fs, $I \approx 10^{14}$ W·cm^{-2}) can be used to directly write 3D modification patterns in a glass exploiting non-linear absorption [27]. The ability to modify refractive index, induce crystallization, or form nanoparticles with large spatial selectivity and control, allows to create structures that add new functionalities to the glass, e.g. for waveguides writing, or glass coloring.

Laser welding of silica glass substrates without the insertion of intermediate absorption layers has been studied by use of near-infrared ultrafast laser radiation ($\lambda = 800$ nm, $t_p = 130$ fs, $f_{rep} = 1$ kHz) [28]. When laser radiation is focused at the interface of transparent materials, the material around the focal point is melted due to the localized nonlinear absorption of optical pulse energy and consequently the temperature increase. This technique has also been applied to the joining of semiconductors such as silicon wafers. Laser micro-welding of materials using ultrafast laser radiation ($\lambda = 1558$ nm, $f_{rep} = 500$ kHz) has been reported on non-alkali alumino-silicate glass substrates [29]. The welding results in a joint strength of 9.87 MPa. Welding of a non-alkali glass substrate and a silicon- substrate also succeeded, resulting in a joint strength of 3.74 MPa.

Melting as well as direct fusion welding of borosilicate glass has been reported by use of high-repetition rate ($f_{rep} = 500\,\text{kHz} - 2$ MHz) picosecond and femtosecond laser radiation [30, 31]. The nonlinear absorptivity of the laser pulses has been determined for different pulse energies, repetition rates, scanning velocities and focus positions. The transient and time-averaged temperature distribution in fusion welding of glass has been calculated using a thermal conduction model where heat is instantaneously deposited at different repetition rates in a solid moving linearly at a constant velocity. Femtosecond lasers with large repetition rates provide an efficient fusion welding, which

melts selectively the joining interface at welding speeds up to $v \approx 100$ mm/s.

Numerical simulations and modeling

Extensive numerical simulations have been carried out in order to investigate the phase transitions during ablation by ultrafast laser radiation. The most common pathways for modeling ultrafast phenomena are given by molecular-dynamics and/or thermodynamic simulations.

Homogeneous nucleation is considered as a mechanism for rapid thermal melting of solids irradiated with ultrafast laser radiation [32]. Modeling based on classical nucleation theory exposes that for sufficient superheating of the solid phase, the dynamics of melting is mainly determined by the electron-lattice equilibration rather than by nucleation kinetics. According to the calculations, complete melting of the excited material volume occurs within a few picoseconds. This time scale ranges between the larger time scale for heterogeneous, surface-nucleated melting and the shorter time scale for possible non-thermal melting mechanisms.

The kinetics and microscopic mechanisms of laser melting and disintegration of thin Ni and Au films irradiated by a single ultra-short laser pulse ($t_p = 200$ fs-150 ps) have been investigated in a coupled atomistic-continuum computational model [33]. The model provides a detailed atomic-level description of fast non-equilibrium processes of laser melting and film disintegration. At the same time, the model ensures an adequate description of the laser light absorption by the conduction band electrons, the energy transfer to the lattice due to the electron-phonon coupling, and the fast electron heat conduction in metals. The relative contributions of the homogeneous and heterogeneous melting mechanisms are defined by the laser fluence, pulse duration, and the strength of the electron-phonon coupling. At large laser fluences, significantly exceeding the melting threshold fluence, a collapse of the crystal structure overheated above the limit of crystal stability takes place simultaneously in the whole overheated region within 2 ps, skipping the intermediate liquid-crystal coexistence stage. Anisotropic lattice distortions and stress gradients destabilize the crystal lattice, reduce the overheating required for the initiation of homogeneous melting down to $T \approx 1.05 \cdot T_m$, and expand the range of pulse durations for which homogeneous melting is observed in 50 nm Ni films up to $t_p = 150$ ps. High tensile stresses generated in the middle of an irradiated film can also lead to the mechanical disintegration of the film.

The reaction of solid matter exposed to ultrafast laser radiation has been modeled hydrodynamically by pointing out the isochoric heating as a driving mechanism for producing highly non-equilibrium thermodynamic states [34, 35]. An estimation of the thickness of the liquid layer, localized between the expanding matter and the unaffected solid substrate, has been performed.