Introduction

The aim of this thesis is to investigate the principal physical processes that determine the practical effectiveness of using lasers for the modification and ablation of solids. The main feature distinguishing the laser from other energy sources is the local character of its action and the easiness of manipulating by optical means. The temporal and spatial coherence of laser radiation enables one to achieve high-power and high energy densities with it. Its narrow frequency distribution provides a means of controlling the process of absorption of radiation by matter.

The term “ablation” refers to macroscopic removal of material when a sample is irradiated with energetic beams.

In this respect it is very important to illustrate the possible different mechanisms that occur when powerful light beams hit solid targets, to assign the observed processes and to underline the possible applications.

The interest in laser ablation of different materials exists from the discovery of the laser in 1960 [Mai60] and the need for optical components resistant to optical damage. Since then powerful beams of light have been directed at solid materials for a variety of purposes. Later in the sixties, the process of laser ablation was studied and roots of the major applications appeared, so one can say the study of the interaction of high-power lasers with solid matter is as old as the laser itself[1]. Lasers have been widely used in industrial scale material processing, cutting, welding, induced oxidation, and annealing and other different types of surface processing. But the use of the laser ablation technique was catapulted into scientific prominence initially by the possibility of using lasers as lithographic tools and then by the developments in the growth of high-T_c superconducting thin films. As versatile sources of pure energy in a highly concentrated form, lasers have become attractive tools and research instruments in metallurgy, semiconductor technology and engineering. Lasers have been successfully employed in material treatment, laser hardening, thin film deposition, new composite materials, high Tc superconductors or materials of biological interest. The increasing availability of ultrashort, sub-ps pulsed lasers is awaking growing interest in material structuring, especially „transparent“ dielectric micromachining. In contrast to the more

[1] See Appendix 1

standard investigations of material ablation, or sputtering, with ns laser pulses, ultrashort pulses have the additional advantage of not interacting with the plume of ablated material since the pulse has stopped before the material removal takes place. The avoidance of secondary effects due to plume heating etc. makes a more detailed investigation and understanding of the fundamental laser-matter interactions and mechanisms of material removal feasible [RAV98]. This is beginning to open the way to a more detailed understanding of energy deposition into the sample and to a real time monitoring of the electronic and atomic processes occurring in solids under ultrashort pulsed laser excitation.

The field of laser-material interactions is inherently multidisciplinary. Upon impact of a laser beam on a material, electromagnetic energy is converted first into electronic excitation (except for MIR radiation that can be efficiently coupled directly into vibrational modes). Then, by specific electron-lattice interactions, the energy is transferred to the lattice, being converted into thermal, chemical and mechanical energy. In the whole process the molecular structure as well as the shape of the material are changed in various ways.

This thesis will follow the trace of the laser energy on interaction with wide band-gap dielectrics on a ps and sub-ps scale from the initial interaction with the electronic system to the delayed deposition into the lattice and material removal. It will identify the processes determined by the local deposition of energy into the sample, which develop into the characteristic phenomenon of ablation, emphasizing the dynamics and the characteristic temporal scale of the processes occurring.

The generally accepted picture for the excitation of dielectrics with ultrashort, near infrared or visible laser pulses is that the initiating excitation mechanism is multi-photon absorption, either from already present morphological or structural defect states in the band gap or by direct interband transitions, which seed additional ionization due to electron impact [DLK94]. This is followed by photoelectron emission with surface charging and thermalization of the quasi-free electronic system on a material-dependent time-scale and energy transfer to the lattice by electron-phonon coupling with subsequent heating of the sample [SAR99]. The questions we have tried to answer refer to how and how long does it take for a particle to be emitted. The approach was to identify the paths and temporal characteristics of the energetical channels originating from the laser beam and coupled with the emitted particle itself. What is the energetic spectrum of the emitted particles? What happens to the surface and to the affected bulk after laser irradiation? To what extent can this micron or sub-micron modification be controlled by an optimal choice of laser parameters? What is the role of laser induced defects in surface micromachining or optical properties of the irradiated solid?

One motivation was found in potential applications such as the structuring of dielectrics or phenomena related to aging of optical components.

The present study focuses mainly on sapphire (c-Al_2O_3) in view of its many useful mechanical, optical and electrical properties (it is often used as an optical material and as a substrate for thin film deposition), and also due to the interesting appearance of different ablation phases upon laser irradiation. A “gentle” phase is found for low laser fluences (and low numbers of laser shots) and characterized by the removal of a few nm in depth per laser shot, leaving behind a smooth surface [ARV97]. Surface charging and ion Coulomb explosion is found to be the initial stage in material removal. The “strong” phase is characterized by an order of magnitude higher ablation rate per pulse, it is accompanied by significant plasma light emission and shows a violent expulsion mechanism tentatively assigned to phase explosion. The dynamics of these processes are followed by the means of pump-probe techniques.

This thesis is structured as follows:

The first chapter introduces a theoretical approach describing the optical absorption in dielectrics and laser energy coupling into the targets, based on optical properties of dielectrics, electronic transitions and relaxation, impact ionization and free electron heating, energy transfer to the lattice by electron-phonon coupling or via selective ways implying defect states formed under the excitation. A rate equation describing the augmentation in the free electron concentration up to the “critical density” is derived. The development of a significant concentration of free electrons leading to enhanced radiation absorption and finally to optical damage is presented. This chapter will also outline some mechanisms of particle emission for sub-ps irradiation compared to the „classical“ ns lasers.

The second chapter presents the experimental setup and the methods used for monitoring the ablation process. The experimental approach involves both ex-situ (microscopy) and in-situ investigations. A time-of-flight mass spectrometer was developed to study particle detection; ions and electrons that have provided evidence for the occurrence of non-thermal processes, and neutrals that are responsible for most of the material being removed under our conditions of laser excitation.

The third chapter deals with the behavior of dielectrics (sapphire, fused silica, and quartz) under laser excitation emphasizing the studies made on sapphire samples as characteristic for most of the transparent materials. The effect of different laser parameters is studied by ex-situ methods: optical inspection and scanning electron microscopy. Different ablation phases are identified as well as the mechanisms responsible.

The fourth chapter continues the discussion on the mechanisms, presenting arguments based on in-situ methods of investigation, mainly time-of-flight mass spectrometry.

The fifth chapter is about the temporal behavior of the laser energy deposition process from the electronic system to the lattice and subsequent particle emission.

Possible applications are presented in Chapter 6 to emphasize the strong potential of ultrashort lasers in the new emerging electronic and information technologies.

To conclude, this thesis provides answers to questions related to the

1) advantage of femtosecond lasers as indispensable tools for basic research in the field of laser-material interactions, the main motivation being the possibility of fully controlling the ablation process and exploring the palette of laser induced effects, from surface patterning to in-volume modifications
2) the involvement of ultrashort pulsed lasers in potential industrial applications, their advent from “exotic” instruments towards high precision micromachining tools for transparent materials, sapphire samples being used as proof-of-principle for the multitude of processes being investigated.