2 Interaction of photons with matter

2.1 Basic principle of photons-matter interaction

Electronic transitions can be induced by the absorption of photons in matter. In particular, the photons can induce transitions from the valence band to conduction band, charge transfers from one constituent to another, or the creation of excitons. From the excited state the electrons relax to a lower energetic state via radiative and non-radiative transitions. Very often non-radiative transitions are dominating.

2.2 Interaction mechanisms of photons with transparent dielectric material

If the bandgap of a dielectric is larger than the photon energy of the incident laser photons no linear absorption of the photons by the valence electrons is possible. Thus, no transitions from the valence band to the conduction band take place. The bandgap of about 9.0 eV of fused silica exceeds the photon energies of conventional UV laser systems which are in the range of 3.5 to 7.9 eV [17, 18]. Two types of mechanisms can describe the interaction mechanisms between UV laser radiation and wide-bandgap materials: nonlinear absorption and defect-induced absorption.

2.2.1 Nonlinear absorption mechanism

A wide-bandgap material free of defects that is transparent at moderate photon flux densities can become opaque at sufficiently large laser intensities because of nonlinear absorption mechanisms, such as multiphoton absorption [17, 19]. A valence electron can be excited to the conduction band by the absorption of two or more photons.

Further, three mechanisms have been proposed to account for the production of a large amount of electrons necessary to cause materials damage: (i) continued multiphoton absorption, (ii) triggered conduction band absorption, and (iii) multiplication by an avalanche process. In the second mechanism, the initially excited electrons in the conduction band due to the multiphoton absorption process can trigger a one-photon absorption for the incidence laser photons and can further increase their energy by intraband absorption [20-22]. In the third mechanism, the existing conduction band electrons are accelerated in the electromagnetic field of
the laser until they reach an energy larger than the energy required for ionization. Hence, they can transfer this excess energy to valence electrons, which are excited to the conduction band. In this manner, a cascade-like amplification process develops. Extensive literature deals with theoretical and experimental studies on both multiphoton absorption and avalanche mechanism (Refs. cited in [17, 19]).

Permanent changes of the optical properties of the dielectric can be attributed to structural damage of the lattice due to nonlinear absorption processes. In particular, the bulk of fused silica is damaged at intensities larger than $10^{13}$ W/cm² [23]. Such large intensities can be achieved usually with femtosecond (fs) or picosecond (ps) laser pulses [17] whereas only $10^7$–$10^9$ W/cm² are typically for nanosecond (ns) laser pulses.

### 2.2.2 Defect-induced absorption

For the defect-induced absorption mechanism the photon-matter interaction occurs indirectly via defect states in the bandgap (intraband states). In general, defects in a dielectric can trap electrons or holes (point defect). Such defects are laser-generated (at sufficiently large laser intensities) or intrinsic defects.

**Laser-generated defects**

Electronic defects can be generated during laser irradiation with large intensities, for instance by multiphoton absorption processes. A few fundamental defects have been identified for fused silica, such as neutral oxygen vacancies. An oxygen vacancy is believed to be a precursor of an $E'$ center (a silicon dangling bond with a trapped hole) and a non-bridging oxygen hole center (NBOHC, an oxygen dangling bond) [24, 25]. These defects have absorption bands at 5.8 eV ($E'$ center) and 4.8 and 6.8 eV (NBOHC). Beside oxygen vacancies also several variants of silicon bond defects (vacancies and interstitials) are possible and exist with certain probabilities and lifetime [26-28]. In some cases, the transient defects become permanent and affect the following laser pulse due to an enhanced absorbance. The accumulation of such defects and, consequently, the increasing of absorbance during prolonged laser irradiation are termed in the literature as incubation [17, 29]. Such radiation-induced defects can cause a structural compaction of the exposed material volume [30].
**Intrinsic defects**

Dielectric materials containing defects are damaged at much smaller laser intensities than a defect-free material. Several kinds of factors affect the absorption of the laser radiation in wide-bandgap materials: (i) preexisting structural defects, (ii) interfaces/surfaces, and (iii) environment. Additionally to laser-generated defects, photons absorption can also be enhanced by preexisting chemical and structural imperfections of the dielectric material. Significantly larger absorption can take place at interfaces or surfaces due to the existence of surface states [31, 32], the presence of topological imperfections [33], and chemical impurities and contaminations [21]. Various means, such as mechanical polishing [34, 35] and γ radiation [36], have been used to create defect states near the surface. With respect to the environment, a gaseous atmosphere in contact with the laser illuminated surface has important effects on the generation of defects [37].

### 2.3 Thermal processes

The primary interaction between photon and matter is always non-thermal [17]. The transfer of energy of the electrons to vibrations of the lattice heats the surrounding matter. The evolution of the temperature in the material due to the absorption of laser energy can be calculated with the heat equation.

#### 2.3.1 Heat equation and definitions

In the most general case, the temperature is a function of both spatial coordinates and time. The temperature evolution depends on the optical absorption of the laser radiation, the heat flux from the irradiated zone, and on transformation enthalpies of phase transitions, such as melting or evaporation.

The one-dimensional heat equation where the spatial coordinate (z-direction) is parallel to the propagation of the laser beam (and vertical to the surface) is appropriate for thermal considerations since the beam size of the laser is usually larger than the characteristic lengths of optical or thermal penetration. Furthermore, the heat transport by convection and thermal radiation is neglected, the material is assumed as uniform and isotropic, and its properties are considered to be independent of the temperature. The linear heat equation extended by a source term \( Q(z, t) \) reads according to [17]:

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} + Q(z, t)
\]
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\[ q \ c_p \ \frac{\delta}{\delta t} T(z, t) - \frac{\delta}{\delta z} \left[ \kappa \ \frac{\delta}{\delta z} T(z, t) \right] = Q(z, t) \],

where \( q \), \( c_p \), and \( \kappa \) are mass density, specific heat capacity, and thermal conductivity, respectively. These coefficients can be combined to the thermal diffusivity:

\[ D = \frac{\kappa}{q \ c_p} \].

The source term is equal to the absorbed energy of the laser irradiation by the material which is totally transformed into heat. According to the law of Lambert-Beer the source term can be written as:

\[ Q(z, t) = (1 - R) \ \alpha \ I(t) \ \exp(-\alpha \ z) \],

with the linear absorption coefficient \( \alpha \) and the laser intensity \( I(t) \). Herein, the reflection losses have been taken into account by \((1 - R)\). Instead of \( \alpha \) sometimes the optical penetration depth \( d_{\alpha} \) is used:

\[ d_{\alpha} = \alpha^{-1} \].

From (2-3) it is obvious that the temporal dependence of the laser-beam intensity \( I(t) \) has a significant effect on the source term and, consequently, on the resulting temperature evolution. To meet the most relevant case for this work a laser pulse with temporally constant intensity and pulse duration \( \tau_p \) is considered:

\[ I(t) = \begin{cases} I_0 & \text{for } 0 \leq t \leq \tau_p \\ 0 & \text{for } t > \tau_p \text{ and } t < 0 \end{cases} \].

In applications of pulsed lasers the energy fluence of the laser pulse (further abbreviated to the laser fluence \( \Phi \)) is often used instead of \( I_0 \) [17]:

\[ \Phi = I_0 \ \tau_p \].

An important parameter in thermal processes is the heat diffusion length or heat penetration depth:

\[ d_T \approx \sqrt{4 \ D \ \ell} \],

which is a measure of the heated material depth as a function of the time. Usually, the laser pulse duration \( \tau_p \) is used to quantify \( d_T \) during the heating cycle of the laser pulse.

2.3.2 Pulsed laser irradiation of semi-infinite substrates

According to [17] for pulsed laser irradiation of plane, semi-infinite substrates
with finite absorption a solution of the heat equation for the heating cycle of the laser pulse \((0 \leq t \leq \tau_p)\) can be given:

\[
\Delta T(z, t) = \frac{I_0}{\kappa} \left\{ d_T \text{erfc} \left( \frac{z}{d_T} \right) - \frac{1}{\alpha} \exp(-\alpha z) + \frac{1}{2 \alpha} \exp \left( \frac{(\alpha d_T)^2}{2} \right) \right\} \cdot \sum_{\pm} \exp(\pm \alpha z) \text{erfc} \left( \frac{\alpha d_T}{2} \pm \frac{z}{d_T} \right).
\] (2-8)

The descriptions erfc and ierfc are the complementary Gauss error function and the inverse complementary Gauss error function, respectively. The specific values of erfc and ierfc are given in mathematical tables [38, 39].

In the following, (2-8) will be discussed considering some boundary values. The heating confinement depends on the material properties. Two cases can be discussed depending on the rate of laser energy dissipation in the sample: (i) thermal confinement and (ii) optical confinement.

(i) In the case of thermal confinement the thermal diffusion length within the laser pulse duration (2-7) exceeds the optical absorption length \((d_T \gg d_\alpha)\). Hence, one can assume for simplification an infinite absorption \((\alpha \to \infty)\) and, therefore, only the first term in the parenthesis of (2-8) remains:

\[
\Delta T(z, t) = \frac{I_0}{\kappa} d_T \text{erfc} \left( \frac{z}{d_T} \right).
\] (2-9)

In particular, in the case of \(z = 0\), i.e., the materials surface, \(\text{ierfc}(z = 0) = \frac{1}{\sqrt{\pi}} [17]\) and (2-9) yields:

\[
\Delta T(z = 0, t) = \frac{I_0 d_T}{\sqrt{\pi} \kappa}.
\] (2-10)

(ii) The temperature distribution in the case of optical confinement \((d_\alpha \gg d_T)\) is caused by a finite penetration of the laser radiation. In the case of \(z = 0\) (2-8) is:

\[
\Delta T(z = 0, t) = \frac{I_0}{\kappa} \left\{ \frac{d_T}{\sqrt{\pi}} \left[ 1 - \exp \left( \frac{(\alpha d_T)^2}{2} \right) \right] \text{erfc} \left( \frac{\alpha d_T}{2} \right) \right\}.
\] (2-11)

At \(t = \tau_p\) (2-11) can be also described by the heat balance if the heat can not flow outside the irradiated volume within the duration of the laser pulse [17]: the absorbed laser intensity heats a material layer of thickness \(d_\alpha\). The so-termed calorimetric solution of the heat equation is:
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\[ \Delta T = \frac{l_0 \tau_p}{q \ c_p \ d_\alpha} . \]  

(2-12)

The cooling cycle of the material after single-pulse irradiation can be described according to [17] by subtracting the solution for the heating cycle starting at \( t = \tau_p \) from the heating cycle starting at \( t = 0 \); i.e., for \( t > \tau_p \):

\[ \Delta T(z = 0, t) = \frac{2 \ l_0 \ \sqrt{D}}{\sqrt{\pi} \ \kappa} \ (\sqrt{t} - \sqrt{t - \tau_p}) . \]  

(2-13)

2.3.3 Phase changes of solid matter

Melting and vaporization

If the laser fluence exceeds the threshold fluence for melting, the temperature evolution can be calculated from the heat equation (2-1) only when the latent heat of melting is considered in the source term [17].

For a solid semi-infinite substrate uniformly irradiated by temporally rectangular laser pulses of duration \( \tau_p \), the temporal behavior of the surface temperature \( T_s \) can be explained according to [17]. Material evaporation shall be ignored at this point. At equilibrium conditions, \( T_s \) reaches the melting point \( (T_m) \) within a time \( \tau_m(0) \). Subsequently, almost no temperature rise occurs because the absorbed laser energy is consumed by the melting, which requires the enthalpy \( \Delta H_m \) per mol. After a time \( \tau_m(h_i) \) the surface is molten to a depth \( h_i \). If \( h_i \) is within \( d_T \) and \( t < \tau_p \) the melt front matches the heat front and \( T_s \) increases further. The maximum in \( T_s \) is reached at \( \tau_p \).

For laser fluences around the melting threshold, the maximum melt depth \( h_{l\text{max}} \) can be approximated from the solution (2-8) considering a large area irradiation and a strong surface absorption of the laser beam by the material [17]:

\[ h_{l\text{max}} \approx \frac{d_T \ \Phi - \Phi_m}{\sqrt{\pi} \ \Phi_m} , \]  

(2-14)

where \( \Phi_m \) is the fluence necessary for surface melting. (2-14) is valid for \( \Phi \approx \Phi_m \). If \( \Phi > \Phi_m \), the solution of (2-8) yields for fluences of \( \Phi - \Phi_m \ll \Phi_m \) [17]:

\[ h_{l\text{max}} \approx d_T \sqrt{\frac{\Phi - \Phi_m}{\Phi_m}} . \]  

(2-15)
Both, (2-14) and (2-15) are only a crude estimation of the melting depth because they present a description of the non-linear melting problem by linear solution [17]. For fluences well above $\Phi_m$, a simple approximation of the maximum melt depth in pulsed laser irradiation is based on the energy balance [17]:

$$h_{m}^{\text{max}} \leq \frac{\Phi_a - \Phi_m}{\varrho \Delta H}.$$  \hspace{1cm} (2-16)

$\Phi_a$ is the absorbed laser fluence and $\Delta H = \Delta H_m + c_p (T_m - T_0)$ the total enthalpy, with $\Delta H_m$ as melting enthalpy of the material.

In contrast to the preceding subsection, in many kinds of laser material processing the heating cycle is very short and heating rates are large. If the degree of overheating is very large inhomogeneous melting within the heated volume of the solid occurs. For high-intensity laser pulses and focused laser-beam irradiation, liquid expulsion and vaporization become important and disturb the equilibrium of the system. Then, the deformation of the surface must be taken into account.

The exact temporal behavior of $T_S$ depends on the material, the intensity distribution, and shape of the laser pulse, the convective heat flows, and the type of the ambient medium. Hence, the total spatial and temporal temperature distribution within the liquid and the solid material can be calculated only numerically [17].

When the laser energy input is large enough to induce significant materials vaporization, a dense vapor plume is formed above the surface. The vapor may consist of clusters, molecules, atoms, ions, and electrons. The composition depends amongst others on the laser intensity, the laser wavelength, the material (composition as well as structure), and the ambient medium. Vaporization takes place when the temperature of the material approaches the boiling temperature $T_B$. When $T_S$ reaches $T_B$ the boiling enthalpy $\Delta H_B$ is required for the vaporization of the material. The strong temperature and pressure gradients in the direction of surface normally cause a strongly forward directed fast expansion of the vapor plume that can be treated as an adiabatic process [17]. In any case, materials leaving the surface generate a recoil pressure on the substrate. In the presence of a molten layer, the recoil pressure partially expels the liquid. The vapor plume may also generate strong shock waves in both substrate and ambient medium [17].

Boiling occurs at that temperature for which the vapor pressure of the substance equals the ambient pressure. Hence, $T_B$ depends on the pressure. Usually, boiling
temperatures are published with respect to standard pressure (101.3 kPa). $T_B$ increases with increasing ambient pressure up to the critical point where the liquid and the gaseous phases become indistinguishable and the material is neither liquid nor gaseous but in the state of a supercritical fluid [40]. In particular, the critical point of the organic solvent toluene amounts at a temperature of 319°C and a pressure of 4.1 MPa [40].

Vitreous materials

If crystallization of a cooling melt is kinetically hindered, vitreous materials are formed by supercooling and freezing-in the molten state [41-43]. The solidification of a glass from a melt is called glass transition. The glass transition is accompanied by a gradual change of linear expansion of the materials volume in the temperature region of the liquid-solid transition (Fig. 2-1). If the thermal history and the cooling rate of the melt are fixed, the transition temperature can be determined by extrapolating the linear expansion of the melt (above transition) and the glass (below transition). The intersection of both extrapolations gives the glass transition temperature $T_g$ (exact measurement according to DIN 52324). In the temperature range between $T_g$ and $T_M$, the state of the glass-forming material is that of a metastable or supercooled melt. At cooling, the atomic mobility becomes smaller and the melt reaches the vitreous state at $T_g$. The glass transition temperature depends on the cooling rate. During fast cooling, the structural units of the melt have less time to rearrange. Therefore, glass transition will be shifted towards larger temperatures in comparison to slow cooling [41, 42]. The same behavior is noticed when the glass is reheated to a metastable or undercooled melt with fast heating.

![Fig. 2-1: Schematic diagram of the volume as a function of the temperature for a glass-forming material. Here, $T_g$ and $T_M$ are the glass transition and melting temperature, respectively.](image-url)
A liquid or melt has a viscosity (\(\eta\)), a measure of its resistance to flow. When a glass-forming material such as silica is cooled, its viscosity normally increases [46]. In particular, at \(T_g\) the viscosity of many glasses is about \(10^{12}\) Pa s [43, 44, 46, 47]. Above this viscosity, the class can be treated as solid.

The heating or cooling rates of most of the conventional glass forming processes at which viscosity matters are in the range of K/min. However, the rate of temperature change in a laser heating process with a 1 \(\mu\)s laser pulse is in the range of \(10^8\) K/s localized in a small materials volume near the surface [45]. Due to the rapid change of temperature with respect to the time scale of structural relaxation, the microstructural state of the glass remains unchanged in the time scale of the laser pulse [43-45, 48]. With nanosecond laser pulses the heating rates are even in the range of \(10^{11}\) K/s while quenching rates amount to about \(10^9\) K/s. The response of vitreous materials on such rapid thermal cycle is very difficult to describe and object of some recent publications [42-45, 48-50].

2.4 Liquids and pulsed laser irradiation

The pulsed laser irradiation of an absorbing liquid induces a broad range of physical effects (as depicted in Fig. 2-2a), such as rapid heating, explosive evaporation, bubble formation, transient pressure generation, bubble collapse, as well as laser-induced chemical processes, e.g., photolysis of molecules of the liquid (Fig. 2-2b), or chemical reactions between molecules and/or photolysis products. To further aggravate the situation, processes interact with each other. Hence, a detailed description of laser-induced effects in a liquid is very difficult.

2.4.1 Physical effects induced by laser irradiation of an absorbing liquid

**Transient pressure generation**

The heating of a free liquid surface (without a solid boundary; see Fig. 2-2a) by a laser pulse induces thermal expansion of the volume of the liquid within the laser radiation is absorbed. This volume initially pushes the surrounding liquid medium and causes a compressive pressure wave, which is directed opposite from the heating zone. Simultaneously, the recoil momentum induces a zone of large pressure inside the heated volume of the liquid.
Simple estimates of the magnitude of pressure due to laser absorption are possible for two limiting cases [51]. In the short pulse range (acoustic penetration depth \(d_{aco} \ll d_\alpha\), with \(d_{aco} = c_5 \tau_p\) and the speed of the acoustic wave \(c_5\)), the volume of the liquid within the laser energy is absorbed cannot expand during the heating cycle. According to Kim et al. [51] the peak pressure \(\Delta p\) for short-pulse limit can be approximated by:

\[
\Delta p \approx \frac{c_5^2 \beta \alpha}{c_p} \Phi ,
\]

(2-17)

where \(\beta\) is the thermal expansion coefficient of the volume of the liquid.

The long pulse range corresponds to \(d_{aco} \gg d_\alpha\). In this limit, the acoustic pulse traverses the absorption zone during the duration of the laser pulse and the peak
interaction of photons with matter

Pressure can be estimated by:

$$\Delta p \approx \frac{c_s \beta}{c_p \tau_p} \Phi.$$  \hspace{1cm} (2-18)

For typical conditions in this presented work ($\tau_p = 25$ ns; $c_s = 13.2 \cdot 10^4$ cm/s, see Table A 2; $\alpha \approx 1700$ cm$^{-1}$, see Table 5.1) the long pulse condition is fulfilled.

**Rapid liquid heating by a short laser pulse**

When a sufficiently large amount of energy is deposited during a short time interval at large laser fluences, substantial overheating of the liquid beyond the standard boiling temperature can be achieved without evaporation [51]. Thus, the state of a supercritical fluid (subsection 2.3.3) can be reached for a short time. However, an “explosive evaporation” may take place subsequently as a result of superheating [51]. The evaporation causes a fast decreasing of temperature and pressure.

**Bubble formation and bubble collapse**

If laser radiation is absorbed in a liquid medium and a sufficiently large number of nuclei for bubble formation are available, vapor bubbles can be formed in the liquid. When these vapor bubbles collapse, liquid rushes towards the center of the former bubble, and the low degree of compressibility of the liquid produces a strong impact launching a compression wave into the liquid. At the end of the collapse cycle, the pressure inside the bubble rapidly increases and a second shock wave is generated. Several oscillations can follow the bubble collapse. The energy of such a spherical bubble collapse is proportional to the incident laser pulse energy [53] and can be approximated by the bubble energy under considering the maximal radius and consequently the lifetime of the bubble [53, 54].

**Bubble collapse at solid-liquid interface**

The bubble collapse near a solid surface, i.e., at the solid-liquid interface, depends strongly on the distance between the bubble center and the solid surface. If the spacing falls below a (empirically determined) specific value of bubble size of $4 \cdot R_{max}$ the bubble migrates towards the solid boundary and changes its spherical shape to become toric. The collapse occurs by the acceleration of the next bubble interface in direction of the solid boundary. This causes a liquid micro jet imping-
ing onto the solid surface. The instantaneous velocity of the jet, $v_{jet}$, can be generally deduced from in situ observations of the bubble formation (e.g., by shadow graph technique [55]). In order to estimate the impact pressure of a liquid jet, the pressure can be calculated with the following formula [53, 55]:

$$\Delta p = q c_S v_{jet}.$$  \hspace{1cm} (2-19)

The high-pressure waves of both the pressure inside the bubble when in contact with the solid boundary and the afterwards impinging liquid jet of about a few hundred MPa are capable to cause an indentation of the surface that can result in permanent materials damage or erosion [53, 55]. The energy of bubble collapse is not alone converted into acoustic energy but also into heat due to the fast compression. From the spectra of luminescence from such laser-created bubbles, transient large temperatures in the range of some 1000 K can be calculated [56].

### 2.4.2 Photochemical processes and effects in absorbing organic liquids

Beside physical effects (subsection 2.4.1), the irradiation of highly absorbing liquids, such as organic solvents and solutions, with light of short wavelengths causes photochemical processes inside the liquid, too [52, 57-59]. Laser-induced photochemistry includes the excitation of molecules, transient photodissociation of molecules, permanent decomposition (fragmentation) of liquid components, or enhancement of chemical reactions between species of the decomposition process. Beside one-step fragmentation processes, such as the UV laser photolysis of benzene derivates with benzyl radicals as transient state of species [52, 58], also a complete degradation of the benzenes into carbon has been observed [57]. The bubble appearance in laser-liquid interactions suggests a gas-phase photolysis due to the laser and chemical reactions of the compounds inside the vapor bubble [59].

The rate equation for a laser-induced photolysis may be very complex [17] because of the multitude of pathways in the photon-induced decomposition of organic molecules [59]. In the case of a single-photon excitation of a single type of reactant, the time-dependent concentration of radicals, $\Pi$, generated in a photochemical reaction of the type $\Pi \text{hv} \rightarrow \Pi + \Pi$ can be given by the diffusion equation according to [17]:

$$\frac{\delta N_\Pi(x; t)}{\delta t} \approx G_{v,\Pi} - J_\Pi - \dot{k}_0 N_\Pi N_{\Pi}$$ \hspace{1cm} (2-20)
with the average number of generated species $\Pi$ per time within the volume of the medium as source term:

$$G_{\nu, \Pi} = \psi \alpha_{\Pi \hat{n}} \frac{I(x, t)}{E_{\nu}}.$$  \hspace{1cm} (2-21)

$E_{\nu}$, $\alpha_{\Pi \hat{n}}$, and $\psi$ are the photon energy of the incident laser beam, the absorption coefficient of the medium $\Pi \hat{n}$, and the quantum yield of the photochemical reaction, respectively. The second term in (2-20) describes the transport of species $\Pi$ by ordinary diffusion out of the irradiated volume and the last term denotes the loss of radicals $\Pi$ by a recombination reaction with temperature-dependent reaction constant $k_0$.

### 2.4.3 Regime of liquid confinement

When an absorbing solid substrate is submerged into a transparent liquid, the initial process of laser ablation is the absorption of light by the solid target. But in contrast to laser ablation in a gaseous atmosphere or vacuum the laser plasma is confined due to the inertia of the liquid. The interaction time and the magnitude of plasma-induced pressure as well as the temperature are enhanced with respect to air at the same laser intensity [60-64]. Hence, the materials ablation rate is highly enhanced by the confinement of the laser plasma due to a liquid and the efficiency for laser material processing is improved.