

# Laser-induced backside wet etching of glasses and crystals

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Symbol	Unit	Annotation
4	2	
$A_S$	$\mu m^{-}$	Spot size of the laser beam at interface solid-liquid
$C_p$	J/(gK)	specific neat capacity at constant pressure and tempera-
Cs	cm/s	Speed of acoustic wave in liquid
d	cm. um. nm	Thickness, length
D	$cm^2/s$	Thermal diffusivity, defined in (2-2)
$d^{I}$	cm. um. nm	Thickness of interface laver
$d_T$	cm. um. nm	Thermal diffusion length, defined in (2-7)
$d_{\alpha}$	cm. um. nm	Optical penetration depth. defined in (2-4)
$E_{u}$	eV	Photon energy
$E_n$	mJ	Energy of the laser pulse
$f_n$	Hz, s <sup>-1</sup>	Repetition rate of the laser pulses
$\Delta h$	nm/pulse	Averaged etch depth per laser pulse
Ι	W/cm <sup>2</sup>	Intensity of the laser beam
I	W/cm <sup>2</sup>	Heat flux density
N		Number of incident laser pulses
n		Refractive index
р	MPa, bar	Total pressure
$R, A, T_{op}, S$		Reflectance, absorbance, transmittance, scattered intensity
t	s, µs, ns	Time
$T; \Delta T$	°C; K	Temperature, temperature difference
$T_{O}$	°C	Ambient temperature, room temperature; 20°C
$T_{C}$	°C	Critical temperature
$T_S$	°C	Temperature at surface $(z = 0)$
Vjet	cm/s	Velocity of liquid jet due to a collapsing vapor bubble
α	cm-1	Absorption coefficient
$\alpha^{I}$	<b>cm</b> -1	Absorption coefficient of the modified interface layer
β	K-1	Coefficient of thermal expansion of the volume
Ε	cm <sup>3</sup> /J	Efficiency of etching; $E = \Delta h / \Phi$ ; etched volume per energy unit
Φ	J/cm <sup>2</sup> pulse	Energy fluence of the laser pulse irrespective of the shape of the laser pulse; abbreviated to laser fluence
$\Phi_{th}$	J/cm <sup>2</sup> pulse	Threshold fluence for a given shape of the laser pulse
К	W/(mK)	Thermal conductivity
λ	nm	Spectral wavelength
$\mu^{\Phi_{th}}$	J-1	Rate constant for the process of surface modification due
		to the deposition of liquids decomposition products to
		describe the incubation effect for the reduction of $\Phi_{th}$
Q	g/cm <sup>3</sup>	Mass density
$ au_p$	ns	Time duration of the laser pulse

# Symbols and abbreviations

Abbreviation	Description
10 20 20	1 2 2 dimonsional
1D, 2D, 3D AEM	1-, 2-, 3-uniferisional
Агм	Argon fluorido
	Charge coupled device
	Diffractive ontical element
fc	Fortosocond
	Full width at half maximum
CC MS	Cas chromatography coupled with mass spectrometry
HoNo	Halium noon
KrF	Krypton fluoride
ΙΕςνι	Laser-atching at a surface adsorbed layer
LISAL	Laser-induced backside wet etching
ΙΙΔΑ	Laser-induced plasma-assisted ablation
NIR	Near infrared spectral region
ns	Nanosecond
ΛΔΕ	Overall etching
ns	Picosecond
RBS	Rutherford backscattering spectrometry
rms	Root mean square
SEM	Scanning electron microscony
IIV	Illtraviolet spectral region
VIS	Visible spectral region
VIIV	Vacuum ultraviolet spectral region
WLIM	White light interference microscopy
XeF	Xenon fluoride
XPS	X-ray photoelectron spectroscopy

Superscripts	Description	
I	Interface	
L	Liquid	
LV	Liquid volume	
S	Solid	

# **1** Introduction

The processing of surfaces for the fabrication of high-end components requires highly accurate etching techniques. In particular microoptical and microfluidic devices afford high quality etching in the micron and sub-micron range of various dielectric materials. Accurate control of the etch depth and a small roughness of the etched surface are indispensable. For the mentioned applications the materials to be etched have to be transparent, such as fused silica and optical crystals.

The microstructuring of various transparent materials can be achieved by conventional processing, e.g., wet, dry, and plasma etching, but these etch processes require photolithographic masking of the material surface [1]. Consequently, these multi-step processing schemes related to semiconductor industries are suitable for mass production but are too inflexible for small-scale production and rapid prototyping. However, laser processing allows the fabrication of complex topographies and the direct writing of surface features [2]. For surface processing, usually laser ablation is chosen particularly with polymers. Here, laser ablation is well suited for producing micron-sized structures and devices but is currently not used for machining optical components into hard optical materials.

Laser ablation has already been used to etch diffractive and refractive microstructures into polymer surfaces [3, 4]. Due to their low absorption for pulsed excimer laser radiation, transparent dielectric materials, such as fused silica, cannot be etched this way. F<sub>2</sub> lasers with large photon energies [5] as well as ultrashort pulse lasers [6, 7] (e.g. femtosecond laser) can be applied to process optically transparent materials by ablation. However, the respective high costs of the available laser systems together with the often poor surface quality limits the utilization of laser processing for fabricating microoptical structures.

Laser processes at interfaces to ambient media different from air or vacuum attain more and more attention in particular for technological, biological, or medical applications. During the past decade a novel class of laser processing techniques - the hybrid laser etching - was introduced that makes use of conventional nanosecond pulsed lasers, e.g. excimer lasers or solid state lasers. Hybrid laser etching exploits the enhanced absorbance at the interface via additional absorbing materials, such as liquids [8], transient plasmas [9], or adsorbed layers [10]. The hybrid laser processing techniques are characterized by small etching threshold fluence and usually a better surface quality, compared to direct ablation. These attributes together with the high flexibility of the laser tool make the hybrid techniques interesting for high-end application and rapid prototyping of optical materials.

A very promising type of hybrid laser processing is the laser-induced backside wet etching (LIBWE). The LIBWE technique causes laser etching at the back surface of the transparent sample, that is in contact with an absorbing liquid [8, 11]. The LIBWE process is characterized by a low threshold fluence (about 0.50 J/cm<sup>2</sup> for fused silica), a small etch depth per laser pulse (1 to 20 nm/pulse), and a small roughness of the etched surfaces (less than 10 nm rms). Different types of glass, fused silica, and optical crystals have been etched with high precision and with little surface contamination [8, 11-13]. The etch mechanism as proposed in the literature comprises several sequential steps including laser-induced heating of the liquid (which in turn heats the solid), softening or melting of the solid material, and erosion of the weakened material layer by mechanical forces, such as shock waves and transient large pressures [8, 14, 15]. Unfortunately, this proposed mechanism does not reflect the real experiments because it does not explain effects like incubation, liquid decomposition, or surface modification that regularly accompany LIBWE [16]. Interface temperature calculations, which are essential when modeling a thermal mechanism, were made regarding the absorbed laser energy in the liquid as the source for the heating of the solid [8, 14, 15]. The calculated temperatures do not exceed the melting point of the respective material during etching. Thus, particular attention is paid to the effect of processing parameters and to parallel and consecutive processes of laser-induced backside wet etching to obtain a more precise description of the LIBWE-inherent etch mechanism.

In this work, a detailed study of the influence of processing parameters on LIBWE will be presented for fused silica and other glasses and crystals. With the results, the etch mechanism together with the main processes of liquids decomposition, surface modification, and incubation are discussed. With a set of optimized parameters, the etching of microoptical structures into fused silica is demonstrated to show the capabilities of LIBWE in application.

# 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/cm<sup>2</sup> [23]. Such large intensities can be achieved usually with femtosecond (fs) or picosecond (ps) laser pulses [17] whereas only  $10^7$ – $10^9$  W/cm<sup>2</sup> 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  $\gamma$  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]:

$$\varrho c_p \frac{\delta}{\delta t} T(z,t) - \frac{\delta}{\delta z} \left[ \kappa \frac{\delta}{\delta z} T(z,t) \right] = Q(z,t) \quad , \tag{2-1}$$

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

$$D = \frac{\kappa}{\varrho \ c_p} \ . \tag{2-2}$$

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:

$$Q(z,t) = (1-R) \alpha I(t) \exp(-\alpha z)$$
, (2-3)

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:

$$d_{\alpha} = \alpha^{-1} \quad . \tag{2-4}$$

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:

$$I(t) = \begin{cases} I_0 & \text{for } 0 \le t \le \tau_p \\ 0 & \text{for } t > \tau_p \text{ and } t < 0 \end{cases}$$
(2-5)

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]:

$$\Phi = I_0 \tau_p \quad . \tag{2-6}$$

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

$$d_T \approx \sqrt{4 D t}$$
 , (2-7)

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  $(0 \le t \le \tau_p)$  can be given:

$$\Delta T(z,t) = \frac{I_0}{\kappa} \begin{cases} d_T \operatorname{ierfc}\left(\frac{z}{d_T}\right) - \frac{1}{\alpha} \exp(-\alpha z) + \frac{1}{2\alpha} \exp\left[\left(\frac{\alpha d_T}{2}\right)^2\right] \\ \cdot \sum_{\pm} \exp(\pm \alpha z) \operatorname{erfc}\left(\frac{\alpha d_T}{2} \pm \frac{z}{d_T}\right) \end{cases}$$
(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 ( $\alpha \rightarrow \infty$ ) and, therefore, only the first term in the parenthesis of (2-8) remains:

$$\Delta T(z,t) = \frac{I_0}{\kappa} d_T \operatorname{ierfc}\left(\frac{z}{d_T}\right) .$$
(2-9)

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

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

(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:

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

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:

$$\Delta T = \frac{I_0 \tau_p}{\varrho c_p d_\alpha} . \tag{2-12}$$

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  $t > \tau_p$ :

$$\Delta T(z=0,t) = \frac{2 I_0 \sqrt{D}}{\sqrt{\pi} \kappa} \left(\sqrt{t} - \sqrt{t-\tau_p}\right) . \qquad (2-13)$$

#### 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  $\tau_m(h_l)$  the surface is molten to a depth  $h_l$ . If  $h_l$  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  $h_l^{max}$  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]:

$$h_l^{\max} \approx \frac{d_T}{\sqrt{\pi}} \frac{\Phi - \Phi_m}{\Phi_m}$$
, (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]:

$$h_l^{\max} \approx d_T \sqrt{\frac{\Phi - \Phi_m}{\Phi_m}}$$
 (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]:

$$h_l^{\max} \le \frac{\Phi_a - \Phi_m}{\varrho \,\Delta H} \,. \tag{2-16}$$

 $\Phi_a$  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.

#### rates [41, 44, 45].

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  $10^{12}$  Pas [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<sup>8</sup> 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<sup>11</sup> K/s while quenching rates amount to about 10<sup>9</sup> 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 laserinduced 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  $d_{aco} = c_s \tau_p$  and the speed of the acoustic wave  $c_s$ ), 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:

$$\Delta p \approx \frac{c_s^2 \beta \alpha}{c_p} \Phi \quad , \tag{2-17}$$

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



Fig. 2-2: a) The various physical effects involved in the pulsed laser-induced ablation of a free liquid surface [51]. b) Photon-induced chemical processes in molecules of liquid benzene derivates [52].

pressure can be estimated by:

$$\Delta p \approx \frac{c_s \beta}{c_p \tau_p} \Phi \quad . \tag{2-18}$$

For typical conditions in this presented work ( $\tau_p = 25 \text{ ns}$ ;  $c_s = 13.2 \cdot 10^4 \text{ cm/s}$ , see *Table A 2*;  $\alpha \approx 1700 \text{ cm}^{-1}$ , 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]:

$$\Delta p = \varrho \ c_S \ v_{jet} \quad . \tag{2-19}$$

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  $\Pi \ \Pi + h \nu \rightarrow \Pi + \Pi$  can be given by the diffusion equation according to [17]:

$$\frac{\delta N_{\Pi}(x,t)}{\delta t} \approx G_{\nu,\Pi} - J_{\Pi} - \hat{k}_0 N_{\Pi} N_{\Pi} , \qquad (2-20)$$

with the average number of generated species  $\Pi$  per time within the volume of the medium as source term:

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

 $E_{\nu}$ ,  $\alpha_{\Pi \Pi}$ , and  $\psi$  are the photon energy of the incident laser beam, the absorption coefficient of the medium  $\Pi \Pi$ , 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  $\hat{k}_{0}$ .

### 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.

# **3** Pulsed laser ablation and etching of fused silica

Material erosion caused by short laser pulses takes place far from equilibrium and may be based on thermal or non-thermal microscopic mechanisms. The term *laser ablation* is preferred because it is less suggestive with respect to the fundamental mechanisms involved in the process [17]. Laser ablation is characterized by the surface-localized deposition of the excitation energy. A crude estimation for the thickness of the layer removed per pulse,  $\Delta h$ , can be made considering the heat penetration depth  $d_T$  (2-7) or the optical penetration depth  $d_{\alpha}$  (2-4) depending on which is larger:

$$\Delta h \approx \max(d_T, d_\alpha) \quad . \tag{3-1}$$

In the case of ultra short pulses with picosecond or femtosecond time duration  $\Delta h$  is given by  $d_{\alpha}$ .

If material erosion is enhanced or only induced by laser activation of gaseous, liquid, or solid etchants the term *laser etching* is preferably used [17]. Usually, laserinduced etching can be explained by a chemical reaction between the laser activated surface material and the etchant species, often described by the reversal of a corresponding deposition reaction. Photochemical dry etching of fused silica has been investigated with hydrogen and various halide radicals. The latter have been usually produced by excitation of precursor molecules and the etch rates are in the range of Angstrom per pulse [17].

Laser ablation with ultraviolet (UV) excimer lasers, vacuum ultraviolet (VUV) lasers, or ultrashort pulse lasers [5-7, 29, 65, 66] are commonly used for direct processing of transparent materials, such as fused silica. Beside laser ablation also laser processing methods which use additional materials or processes to enhance the absorption of the transparent material at the surface for etching (hybrid laser processing) are objects of recent investigations [8, 10, 67, 68].

# 3.1 Direct laser ablation

Conventional nanosecond UV laser ablation is usually applied for processing of polymer materials. Dielectric materials, such as fused silica, cannot be ablated as well as polymers due to the small absorption of pulsed excimer laser radiation by the material (section 2.2). Ihlemann et al. [29, 65] report on successful ablation of fused silica with ArF and KrF excimer lasers at large laser fluences (about 10 J/cm<sup>2</sup>) with ablation rates of a few hundred nanometers per pulse. At these large fluences a large microroughness is formed and a significant amount of ablation products (debris) is visible around the ablation groove. This suggests a substantial heating of the substrate combined with explosive evaporation [69]. As possible mechanism, the enhancement of absorbance caused by laser-generated and intrinsic defects due to prolonged pulsed laser irradiation (also called incubation) is proposed [29, 65, 69].

VUV F<sub>2</sub> lasers ( $\lambda$  = 157 nm,  $E_v$  = 7.9 eV) can be used for direct ablation of fused silica with a high quality of processed surface, moderate ablation rates (tens of nm), and small threshold fluences (smaller than 1.00 J/cm<sup>2</sup>) [5]. The sufficiently large linear absorption of fused silica for the laser wavelength is attributed to an absorption band with excitation energies below 7.0 eV due to intrinsic and lasergenerated defects (subsection 2.2.2).

Picosecond (ps) and femtosecond (fs) lasers with near infrared (NIR) wavelengths can be employed for ablating fused silica [6, 7, 66] due to multiphoton or defectinduced absorption processes (subsection 2.2.1 and 2.2.2) induced by the large laser intensities (larger than  $10^{11}$  W/cm<sup>2</sup>). A wide range of ablation depths per laser pulse (µm to nm) and medium threshold fluences (about 2.50 J/cm<sup>2</sup>) are determined but the processed surfaces are often uneven and rough due to the formation of ripple structures [6, 7, 66].

# 3.2 Material-assisted backside laser etching

Conventional excimer lasers with ns pulses are employed in hybrid laser etching methods. A sufficiently large absorption of the UV laser wavelengths is provided locally at the materials surface by temporary plasmas [67], adsorbed organic layers [10], or organic liquids [8, 68]. In the principal experimental arrangement of hybrid laser etching the incident laser beam penetrates the transparent sample without significant loss and is absorbed by the absorbing additive on the back surface of the sample (Fig. 3-1a-c). The materials erosion is termed as etching because without the absorbing additive no laser-induced materials erosion occurs at the applied experimental parameters. Otherwise, without the laser the "etchant" is not



c)

capable to etch the material.

Zhang et al. report on *laser-induced plasma assisted ablation* (LIPAA) [67] that exploits a laser-induced plasma as absorbing additive (Fig. 3-1a). The laser pulse generates the plasma due to ablating a metal target beneath the transparent sample. The charged plasma species induces defects in the transparent material, enhances its absorbance for the still incident laser pulse, and an ablation of the modified surface layer takes place. Beside the charged species also deposits of neutral plume species (atoms or clusters) takes place that affects the subsequent laser pulses.

Zimmer etal. introduced the *laser etching at a surface adsorbed layer* (LESAL) [10] that uses an absorption of the laser photons by a thin adsorbed layer of organic solvent on the back surface of transparent materials (Fig. 3-1b). LESAL-processing of fused silica possesses small threshold fluences (smaller than 0.75 J/cm<sup>2</sup>) and offers a certain laser fluence range with a constant etch depth per pulse in the range of 1 nm/pulse.

In 1999 the group of Yabe and Niino [8] introduced hybrid laser etching by means of absorbing organic liquids called *laser-induced backside wet etching* (LIBWE). The influence of experimental parameters on etch rate, morphology, and structural and chemical properties of etched surfaces were investigated for a number of transparent dielectric materials [8, 13, 16, 68, 71-74]. Recently, the use of femtosecond laser pulses in conjunction with LIBWE was successfully demonstrated [75, 76]. The application of established laser processing techniques [2, 17] in conjunction with LIBWE was employed to fabricate well-defined binary and high quality 3D-microstructures, large aspect ratio microtrenches, and periodical submicron gratings into surfaces [72, 77-82]. First in situ investigations of the LIBWE-process were performed by means of time-resolved shadowgraph technique to observe bubble formation [83, 84]. Furthermore, the direct measuring of the transient pressure with a fast-response pressure gauge was applied to estimate initial pressure in dependence on the laser fluence [85].

## 3.3 Proposed thermal mechanism of LIBWE

LIBWE with ns UV laser pulses takes place due to the intensive deposition of energy within a small volume of the liquid [8, 72, 73] that is defined by the spot size of the laser beam and the optical penetration depth of the laser radiation in the liquid. The temperature of the solid rises due to a heat transfer from the hot liquid. When the surface temperature exceeds a critical temperature, the materials surface melts or softens. Due to the simultaneously induced transient large pressure of the liquid (subsection 2.4.1) the molten or softened layer is expelled [8, 72, 73].

In the literature, the melting temperature of cristobalite  $T_m = 1720^{\circ}$ C is proposed as the critical temperature ( $T_c$ ) in the materials removal due to LIBWE of fused silica [8, 14, 15]. Beside  $T_m$ ,  $T_g$  is also a possible critical temperature for etching because of the gradual change of the thermodynamic properties of material, e.g., volume or viscosity, near the glass transition. Otherwise, at  $T_g$  fused silica has still a high viscosity (about  $10^{12}$  Pa s, see 2.3.3) and the material is more a solid than a liquid. Thus,  $T_m$  seems more plausible than  $T_g$  and is further used as  $T_c$  for materials erosion at LIBWE analogous to the literature [8, 14, 15] but without an imperative justification.

In the pioneering work of Wang et al. [8] the temperature of the volume of the liquid was calculated with the calorimetric solution of heat equation (2-12). In the approximation, the laser pulse energy is converted entirely into heat, the liquid is in the superheated state without evaporating (subsection 2.4.1), no thermal conduction out of the irradiated liquid volume takes place, and the temperature of the surface of the solid equals the liquid temperature. For the interface between fused silica and 0.4 mol/l solution of pyrene in acetone, the temperature rise of the liquid volume at etching threshold fluence was calculated to about 2000 K [8, 12]. The calculated temperature of the liquid may exceed  $T_c$  but, due to the approximations, the calorimetric approach in (2-12) presents only a strong simplification of the heating process at solid-liquid interface.

Vass et al. performed numerical simulations of the temperature evolution at LIBWE [15, 73]. The one-dimensional heat equation was solved, including the melting of the solid surface and temperature-dependent physical properties. The absorbed energy of the laser pulse causes a large temperature rise in the liquid on a nanose-cond time scale. Simultaneously, a partial heat flux into the near surface region of fused silica rises its temperature [15, 73]. But the calculated maximal surface temperature of fused silica at the experimentally found etching threshold fluence is distinctly smaller than  $T_c$  [15].

Zimmer etal. suppose in their extended calorimetric approach a laser heated volume with uniform temperature in both the liquid and the solid region that is limited by the respective thermal diffusion lengths [86]. The energy for heating of this volume is equal to the absorbed laser energy within the thermal diffusion length of the liquid. It is further assumed that the laser pulse energy absorbed outside this liquid volume does not contribute to the heating of the solid region. According to [86] and (2-12), the increase of the temperature is given by:

$$\Delta T = \frac{\Phi(1 - \exp[-\alpha^L d_T^L])}{\varrho^S c_p^S d_T^S + \varrho^L c_p^L d_T^L} .$$
(3-2)

The superscripts *L* and *S* describe the materials properties of the liquid and the solid, respectively.

With (3-2), the temperature rise of the interface region of fused silica and 0.4 mol/l solution of pyrene in acetone can be estimated for the threshold fluence of 0.24 J/cm<sup>2</sup> [8] (*Table A 1, Table A 3,* in Appendices) to 470 K. Both, the numerical simulations [15] and the extended calorimetric approach [86], do not deliver sufficiently large surface temperatures for the proposed thermal etch mechanism.

Kawaguchi et al. [85] and Vass et al. [15] estimated from direct pressure measurements and numerical calculations, respectively, the pressure of the laser-irradiated liquid at the solid surface to about 50 MPa (for the etching threshold fluence). This agrees within a factor of two with the approximations that can be made by (2-18) (subsection 2.4.1). For typical conditions in this presented work ( $\tau_p = 25$  ns;  $\Phi = 0.30$  J/cm<sup>2</sup>; toluene:  $c_S$ ,  $\beta$ ,  $c_p$ ; see *Table A 2*,  $\alpha \approx 1700$  cm<sup>-1</sup>; see *Table 5.1*) the pressure increase can be estimated to about 120 MPa. In former work [14, 83], the vapor bubble collapse and the impinging liquid jet is proposed as the mechanism of materials erosion. But numerical calculations [15] show that the largest temperature and pressure occur in the time range of the laser pulse duration and the cooling of the surface starts immediately after the laser pulse. Consequently, the large pressure of the liquid jet (about 200 MPa) only acts on the already cooled fused silica surface due to the bubble lifetime in the range of hundreds of microse-conds [83-85]. Additionally, the high quality of the etched surface and the well-defined patterns with a lateral resolution smaller than 1 µm [72, 77-82] except the localized impact of a micro jet from bubble collapse (see also chapter 9).

The current mechanism of LIBWE together with the temperature calculations gives no unambiguous argument of a softened or molten surface at the threshold fluence for etching. Thus, the estimated pressure of the liquid at the interface cannot mechanically expel the materials surface because it does not exceed the compressive strength of fused silica (*Table A 1*).

# 4 Experimental

# 4.1 Systems engineering

## 4.1.1 Laser workstation and laser

For the experiments a commercial workstation from Exitech Ltd. (Series 7000) has been used. The essential components of the workstation are depicted in Fig. 4-1. The laser workstation is equipped with an excimer laser (LPX 220i Lambda Physik), beam shaping and homogenizing optics, and a dielectric attenuator. An x-y-z stage enables program controlled positioning and scanning of the laser beam across the sample surface with a resolution of 1  $\mu$ m and a maximal velocity of 100 mm/s.

The used laser system (specifications are described in *Table 4.1*) can run with different gas mixtures capable to emit different wavelengths. Significant characteristics are its energy pulse-to-pulse stability and maximal pulse repetition rate. The energy monitor (Fig. 4-1) provides information on the current laser pulse fluence and may, depending on the control mechanism, adjust the discharge voltage of subsequent laser pulses. The operation mode of excimer lasers has been extensive-



BA beam attenuator BD beam diagnostics beam expander beam homogenizer cylinder lens dielectric mirror DM EC LIBWE etch chamber excimer laser energy monitor field lens imaging objective motorization MP mask pattern personal computer surveillance camera WP work piece work piece chuck

Fig. 4-1: Schematic set-up of the laser workstation.

ly described elsewhere [87].

With the cylinder lens (CL), the difference in the dimension of the laser beam in vertical and horizontal direction is initially compensated. The beam attenuator (BA) allows the defined control of the laser pulse energy and consequently the laser fluence on the sample. A beam expander (BE) adjusts the two-axis divergence of the laser beam into the beam homogenizer. The beam homogenizer (BH; either bi-prism or fly's-eye type) transforms the raw excimer laser intensity distribution into a laterally homogenized flat top profile. The additional beam divergence caused by the homogenizing optics is compensated by a field lens (FL). The homogenized beam with a typical energy deviation of 5% rms usually irradiates an area of approximately  $(20 \cdot 20) \text{ mm}^2$  in the object plane or on the mask.

The mask (MP) shapes the laser beam profile for machining. The samples to be machined are irradiated through chromium-on-quartz masks and a variable aperture. The chromium-on-quartz masks are fabricated with electron beam lithography and wet chemical etching. The aperture consists of four blades capable to generate rectangular or square images. The closing and opening of the aperture is motorized and computer-controlled.

The imaging objective (IO) projects the mask onto the work piece. Either a reflective objective (15x demagnification, Schwarzschild-type) or a refractive objective (5x demagnification) is used featuring a resolution of 1.5 and 5  $\mu$ m, respectively.

The position and motion of the work piece (WP) can be controlled by an *x*-, *y*-, and *z*-handling system. In addition, the software gives full control over the handling systems. The work piece as well as the mask positioning systems, the number of applied pulses, and the laser fluence selected by the beam attenuator can be selectively set. For convenience, a unit for beam diagnostics (BD) and an online surveil-

			•	
Laser medium		ArF	KrF	XeF
Wavelength of the laser pulse, $\lambda$	(nm)	193	248	351
Photon energy, $E_V$	(eV)	6.4	5.0	3.5
Max. energy of laser pulse, $E_p$	(mJ)	275	450	200
Max. pulse repetition rate, <i>f</i> <sub>p</sub>	(Hz)		200	
$ au_p$	(ns)		25	
Pulse-to-pulse stability	(±%)		5	
Beam dimensions	$(mm^2)$		(5-12) · 23	

Table 4.1: Specifications of excimer laser LPX 220i from Lambda Physik

#### lance camera (SC) are installed.

#### 4.1.2 Etch chamber

A simple laser etch chamber in the style of the principal experimental arrangement of LIBWE, as shown in Fig. 3-1c, was designed and fabricated (see LIBWE etch chamber in Fig. 4-1). Samples with a diameter and thickness of up to 50 mm and 5 mm, respectively, can be assembled in the chamber. In contrast to the sketch in Fig. 3-1c, the sample surface is aligned horizontally – normal to the vertically incident laser beam (Fig. 4-1). The chamber is made of Teflon to provide for chemical resistance against a wide range of organic chemicals. The absorbing liquids are filled into the cavity which is sealed once by the sample and on the other side by simple screws. After filling the chamber is fixed on top of the positioning stages.

## 4.1.3 Samples: solids and liquids

For the studies, fused silica (Suprasil, Heraeus, USA) was used as standard material. Fused silica glass is an appropriate material to study laser-induced backside wet etching because of its well-known specific physical and chemical properties, e.g., high transparency in UV and VIS, chemical resistance, simple chemical structure, and thermal stability. Samples cut from wafers polished on both sides with a thickness of 380 µm and a surface roughness of about 0.3 nm rms are used as received from clean room package of the manufacturer. The radiation at wavelengths larger



Fig. 4-2: Absorption spectrum of a 0.5 mol/l solution of pyrene in toluene (left axis) and the spectral transmittance of a 380 µm thick fused silica sample (right axis) in the UV spectral range.

than 195 nm is – ignoring reflection losses - totally transmitted by the employed fused silica samples (Fig. 4-2). The absorption edge of the respective samples is at about 165 nm [88]. Beside fused silica, technical glasses from Corning Inc. (Pyrex, 7059) and Schott Group (D263, BK7) as well as optical crystals from Crystec GmbH (quartz, MgF<sub>2</sub>, CaF<sub>2</sub>, sapphire) are applied. Some important material properties are listed in *Table A 1* and *Table A 4*.

To study the LIBWE process, organic solutions and pure organic solvents are used as liquids to absorb the incident laser radiation. All chemicals (with a 99.5% purity) are purchased from Merck KgaA, Germany. In the experiments, solutions of the organic dye pyrene dissolved in toluene are applied as standard absorber with high absorption in the UV (Fig. 4-2). The solutions are made with different concentrations of pyrene up to 0.5 mol/l at which the solution becomes saturated. Beside toluene, xylene, acetone, and acethylacetone are used as well as the halogenated solvents chlorobenzene (C<sub>6</sub>H<sub>5</sub>Cl), dichlorobenzene (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>), and fluorobenzene (C<sub>6</sub>H<sub>5</sub>F). Important liquid properties are listed in *Table A 2* and *Table A 3*.

# 4.2 Laser techniques for microstructuring

The micrometer-to-nanometer controlled, direct material erosion by excimer lasers is employed as a universal manufacturing tool for a wide range of materials [17, 65, 89]. Laser microprocessing can be performed, for instance, by projection the laser radiation via a mask, by direct writing, or by the interference of laser beams (Fig. 4-3). By applying specific masks, such as contour, gray scale, and hybrid masks together with appropriate high precision work-piece positioning the fabrication of real 3D-structures with high precision and small roughness values is possible [13]. The laser fabrication techniques relevant for the experiments will be discussed in the following list.

#### a) Stationary mask projection method (Fig. 4-3a):

The simple method for excimer laser machining uses one or a set of contour masks containing the complete 2D-shape of the area to be irradiated. The projection of laser light shaped by a mask [90] allows binary material processing with a single or a few laser shots. A step-and-repeat process may achieve a patterning of large areas with repetitive elements. In this work, the stationary mask projection is used in principle by projecting the aperture (square shaped) for the etch rate investiga-
#### tions (chapter 5).

#### b) Direct writing with small spot laser beams (Fig. 4-3b):

The scanning of a small laser spot along a designed path across the work piece can produce a 3D-structure. The number of overlapping laser pulses of all successive scans defines the final etch depth. Usually, the patterning is accomplished by translating the substrate with respect to the fixed laser spot. This flexible approach can handle CAD data, but it is rather slowly and produces in the case of laser ablation a crude and rough surface. The direct writing with small laser spots is usually realized with a Gaussian laser beam profile [91]. The application of LIBWE processing in conjunction with small spot writing is executed by projecting a small mask.



Fig. 4-3: Overview on excimer laser microfabrication techniques based on mask projection [2]: a) stationary mask projection, b) direct writing with small spot, c) scanned contour mask, and d) laser beam interference by phase mask projection.

#### c) Scanned contour mask (Fig. 4-3c):

The contour mask shape defines the topographic profile when a contour mask is scanned along a path. In this case different mask regions account for different numbers of overlapping laser pulses which in turn determine the locally etched depth. Hence, the shape of the contour mask is transferred into a depth profile. Following this approach real 3D-microstuctures of high quality can be produced continuously in a time-efficient manner [2]. Intersecting single scans increase the variety of structures that can be fabricated (e.g., periodic morphology). In subsection 9.2.1, the fabrication of a microprism array with a scanned contour mask is demonstrated.

## d) Beam interference by phase mask projection (Fig. 4-3d):

An optical grating splits the laser beam into different orders of diffraction. The 1<sup>st</sup> orders of diffraction interfere on the work piece surface due to the projection by an objective. A special aperture blocks the 0<sup>th</sup> and larger orders. When the intensity at the maxima of the resulting submicron interference pattern locally exceeds the threshold intensity, material erosion starts.

Phase gratings, usually with a binary square wave profile, are designed in order to suppress the 0<sup>th</sup> diffraction order and to maximize the intensity in the ±1<sup>st</sup> orders of diffraction [2]. Providing a line-trench ratio of 1, the diffracted intensity in the 1<sup>st</sup> order is given by  $I_{1^{st}} = I_0 4\pi^{-2} \sin^2(\delta/2)$ .  $\delta$  is the phase shift occurring at the trench depth *d* depending on the refractive index *n* of the gratings material. The phase shift  $\delta$  is defined by  $\delta = 2\pi d (n-1)/\lambda$ . For maximal  $I_{1^{st}}$ ,  $\delta$  must become  $\pi$ .

In this presented work, the fabricated phase grating must have a grating period of  $22 \ \mu m$  and a depth of about 244 nm due to the overall optical set-up of the laser workstation and the laser wavelength. It was etched into fused silica by laser patterning of a photo resist and transferring the resist mask pattern into the substrate by reactive ion beam etching to the desired depth. The period of produced interference pattern employing a reflective objective (15x demagnification, Schwarzschild-type) is calculated to be about 730 nm.

# 4.3 Measurement instrumentation and analytics

# 4.3.1 Scanning and transmission electron microscopy

The etched pits were examined with a JSM 6600 scanning electron microscope (SEM) from JEOL (Japan). Top-view SEM images with a minimum lateral resolution of 10 nm were made by detecting the secondary electrons. Particles from liquid decomposition were dissected and imaged with a JEM 4010 (acceleration voltage 400 kV) transmission electron microscope (TEM) from JEOL (Japan) with a point-by-point resolution of 0.16 nm. The samples were prepared by deposition on LA-CEY carbon film.

# 4.3.2 White light interference microscopy

The principle of white light interference microscopy (WLIM) is described in detail in Ref. [92]. The depth of etched pits and the respective surface roughness were measured with a white light interference microscope Micromap 512 from ATOS with an objective with a magnification of 20x. The depth resolution was better than 1 nm. The roughness of the etched surface was determined with an objective with a magnification of 50x at monochromatic illumination. Due to the wavelength of about 550 nm used in this optical measurement the lateral resolution was slightly less than 1  $\mu$ m. Hence, the cut-off wavelength of the measured surface roughness was in the same range and therefore the method gives no information on the microroughness caused by shorter waviness.

## 4.3.3 Atomic force microscopy

The etched surfaces were additionally investigated by atomic force microscopy (AFM) [93, 94] employing Tapping Mode<sup>TM</sup> [95]. The main advantage of AFM is its sub-nanometer resolution in a scan area up to 100  $\mu$ m × 100  $\mu$ m by giving a direct real space image of the surface. The measured data presented in this work were obtained with a Dimension 3000 stage with a Nano Scope IIIa controller from Vee-co Instruments [95]. All the measurements were performed in air applying silicon tips with a nominal radius smaller than 10 nm and sidewall angles of 18°. For characterizing the surface roughness the root mean square (rms) fluctuations of the height profile h(x,y) [96] were analyzed:

$$rms = \sqrt{\frac{1}{N_P} \sum_{i=1}^{N_P} [h(x, y) - \bar{h}]^2} \quad .$$
(4-1)

Here  $\overline{h}$  represents the mean height of the surface and  $N_p$  the number of points. For a quantitative analysis of the surface roughness scan sizes of  $(2 \cdot 2) \mu m^2$  were used with 512 · 512 points.

## 4.3.4 Gas chromatography coupled with mass spectrometry

The irradiated liquid samples from which solid particles were removed on a centrifuge were analyzed on an Agilent-GC (6890N with the column HP5ms) ion trap system with mass-selective detector (5973) from Agilent Technologies, USA. 0.1  $\mu$ l of the solutions were injected into the system and the different substances were separated by gas chromatography (3 min 40°C - 10 K/min to 280°C - 3 min 280°C) and identified by the retention times and their mass spectra.

#### 4.3.5 X-ray Photoelectron Spectroscopy

The X-ray Photoelectron Spectroscopy (XPS) equipment consisted of an X-ray source with Mg/Al twin anode and a concentric hemispherical electrostatic energy analyzer (VG Microtech CLAM-2) and was mounted on a UHV vacuum chamber with a base pressure of less than  $10^{-9}$  mbar. For the investigations, Al K $\alpha$  radiation (1486.6 eV) was utilized. The core levels of Si 2p, C 1s, and O 1s were measured with 20 accumulations and a point distance of 0.1 eV. The spectra were corrected, analyzed, and fitted by employing the program UNIFIT 3.2 [97].

#### 4.3.6 Raman spectroscopy

Raman spectra had been measured with DILOR XY800 spectrometer (JY Inc., Edison) of the University of Leipzig with a spectral resolution smaller than 4 cm<sup>-1</sup>. The 514.53 nm line of an Ar<sup>+</sup>-ion laser was used to excite the samples with a laser spot diameter of 1  $\mu$ m.

#### 4.3.7 Rutherford backscattering spectrometry

The Rutherford backscattering spectrometry (RBS)/channeling measurements were performed at the HVEE Gonio 941 chamber at the ion beam laboratory LIP-SION of the University of Leipzig [98] with a 2 MeV helium ion beam of 0.8 mm diameter. For RBS/channeling measurements it is imperative to use crystalline

samples (e.g. quartz). The ion beam was aligned parallel to the (0001)-axis of the quartz crystal to ensure deep penetration of the probing ions (channeling alignment). The distinction of the amorphized surface layer due to the laser etch process from the bulk crystalline substrate was possible by comparing the received spectrum with a spectrum on a non-etched region of the sample. The thickness and composition of the amorphous surface layers were determined from the RBS spectra after subtraction of the RBS spectrum from the non-etched region with the RBS simulation code RUMP [99].

#### 4.3.8 Reflectance measurements

A home-made pump probe set-up [100] is realized to investigate reflectance changes at laser-irradiated solid-liquid interface (Fig. 4-4). A lens (8x demagnification) projects a square mask with a size of  $(720 \cdot 720) \,\mu\text{m}^2$  onto the back surface of fused silica samples (thickness: 1 mm). Pure toluene is used as liquid absorber.

The KrF excimer laser worked as "pump source" to initiate the LIBWE process. A continuous wave (cw) fiber-coupled semiconductor laser (23 mW,  $\lambda$  = 810 nm) is used as probing light source with an incident angle of 45° with respect to the normal of the surface. The power stability of the laser diode is estimated to be ±5% at room temperature. The fiber output aperture of the probing laser is projected onto the sample back surface by a lens forming an elliptic spot with a size of about



Fig. 4-4: Experimental set-up of reflectance measurements [100].

450  $\mu$ m at short axis (FWHM). The specular reflected light is focused onto a Si pin photodiode. A digital storage oscilloscope (Tektronix TD5520D) with a sampling rate of two Giga-Samples per second is used to record reflectance signals. Due to the very small difference in refractive index between fused silica at 810 nm (*Table A 1, Table A 2*) the initial reflectance of the solid-liquid interface is calculated according to the law of reflection [101] to about 0.02%. Consequently, the high impedance input of the oscilloscope must be used to achieve a sufficient signal-to-noise ratio.

## 4.3.9 Optical spectroscopy

Optical spectra are recorded on a Shimadzu UV-2101PC UV/VIS scanning spectrophotometer (Kyoto, Japan) in the wavelength range of 190 nm to 900 nm. The spectra are analyzed with Personal Spectroscopy Software UV-2101PC version 3 of Shimadzu. Optical spectroscopy is applied to determine the extinction and consequently the absorption coefficient of organic solvents and solutions in the UV (scanning range: 190 nm - 360 nm,  $\Delta \lambda = 0.1$  nm).

Transmission spectra of laser-irradiated fused silica samples are recorded within a scanning range of 200 nm to 800 nm with  $\Delta \lambda = 0.5$  nm. The sample and the reference light path are masked by an aperture with a diameter of 2 mm because of the limited processable area (spot size of the laser, see subsection 4.4.3). The measured transmission spectra of pristine and unmasked fused silica samples have a precision of ±0.011 (corresponds to a transmittance of 1.1%). Due to the small intensities as result of masking the accuracy of the measurements is reduced. The precision is estimated by iterative measurements with ±0.03 (corresponds to a transmittance of 3%). For calibration, similar pristine fused silica samples are used as reference. An integrating sphere assembly ISR-260 of Shimadzu is installed in the spectrometer to measure the total transmittance of the samples. In this way, the entire transmitted light of a sample is received including the diffusely transmitted light as result of scattering due to enhanced surface roughness.

# 4.4 Sample preparation

#### 4.4.1 Quantification of the etch behavior

The depth of etched pits and the respective surface roughness are measured with WLIM (subsection 4.3.2). Generally, laser exposure at every parameter set is re-

peated three times and the mean value of the etch depths and the roughness is calculated. The y-error bars in the respective graphs present the minimum-maximum deviation of the measured values from the average one (precision). To quantify the etching process, the averaged etched depth per laser pulse  $\Delta h$  (analogous the thickness of the layer ablated per laser pulse; (3-1)), is calculated from the final depth of the etched pits.  $\Delta h$  determined in this way represents an averaging for all applied laser pulses.

#### 4.4.2 Definition of parameter sets for the experimental investigations

In the experiments concerning the influence of relevant processing parameters on the etch behavior (chapter 5), a fixed set of parameters is systematically used. In specific investigations, some of the parameters are altered which is noted in the text or in the figure captions. The main part of the experiments in chapter 5 is done with a 0.5 mol/l solution of pyrene in toluene as absorbing liquid. Toluene as solvent and pyrene dye to raise absorbance is a suitable absorbing liquid to study fundamentals of the LIBWE process (Fig. 4-2). The high absorbance in UV, good solubility for UV active dyes like pyrene, easy handling, and good former experimental results [13, 83] are the reasons for selecting toluene.

In most of the experiments, the spot size of the laser beam is set to  $(100 \cdot 100) \mu m^2$ by the projection of the variable aperture with the 15x reflective objective. The excimer laser runs at  $\lambda = 248$  nm and with a repetition rate of  $f_p = 10$  Hz. The sample and the laser beam are not moved relatively to each other, i.e., no scanning is applied.  $\Delta h$  is investigated as a function of the laser fluence for a fixed set of laser pulses. For  $\Phi < 1.50$  J/cm<sup>2</sup>, 300 pulses are applied. For larger fluences, the pulse number is reduced to 30 to avoid materials cracking [102]. The dependence of  $\Delta h$ on the quantity of applied laser pulses (section 5.2) is examined in the range of 1 to 4000 pulses. Chromium-on-quartz square masks with side lengths from 20  $\mu$ m to 650  $\mu$ m are used to vary the spot size of the laser (section 5.3).

The laser fluences are determined by calorimetric measurements of the laser pulse energy divided by spot size of the laser beam in the projection plane. The precision of estimation of the fluence can be specified for  $\Phi = 5.00 \dots 1.00 \text{ J/cm}^2$  with  $\pm 0.10 \text{ J/cm}^2$  and for  $\Phi < 1.00 \text{ J/cm}^2$  with  $\pm 0.01 \text{ J/cm}^2$ . The laser fluences are estimated taking into account the reflection losses at the first air-silica interface.

After LIBWE processing, the samples are cleaned ultrasonically in a bath of acetone to remove residues of the absorbing liquids and from liquid decomposition. In addition, a heavy adherent carbon-rich film can cover the bottom and the surrounded rim of the etched pit. To remove the layer, the samples are cleaned with a gentle and selective microwave-stimulated oxygen plasma etching process employing a Panel 450 plasma etcher (Leybold AG, Alzenau). The samples are processed for 10 minutes (Helicon-Power: 500 W, Bias-Power: 250 W, 100 sccm O<sub>2</sub>, pressure: 0.5 Pa) without a significant increase of the temperature of the sample. In this process, the etch rate of carbon contaminations is more than 1000 times larger than the etch rate of the fused silica sample. Thus, no alterations of the etch depth by the cleaning procedure can be expected. For SEM and interference microscopic investigations, the samples are coated with a thin gold layer (about 20 nm). The coating is necessary to avoid charging effects during SEM and measurement artifacts when applying WLIM.

## 4.4.3 Sample preparation for analytics

The excimer laser runs at  $\lambda = 248$  nm and at  $f_p = 10$  Hz. A solution of pyrene in toluene (0.5 mol/l) has been used as absorbing liquid. The minimum areas to analyze the surface of the LIBWE-processed samples by means of ellipsometry, optical transmission spectroscopy, RBS, and XPS are about  $(3 \cdot 3)$  mm<sup>2</sup>,  $(3 \cdot 3)$  mm<sup>2</sup>,  $(1.5 \cdot 1.5)$  mm<sup>2</sup>, and  $(8 \cdot 8)$  mm<sup>2</sup>, respectively. The maximal area to be etched by the projection of a single mask is  $(3 \cdot 3)$  mm<sup>2</sup>. For the XPS investigations, a  $(4 \cdot 4)$  array of similar areas is etched by repeating a laser spot with a dimension of  $(2 \cdot 2)$  mm<sup>2</sup>. A  $(100 \cdot 100) \mu m^2$  mask is used for the sample preparation for Raman spectroscopy. After processing, the samples are cleaned ultrasonically in an acetone bath and dried in a nitrogen stream. For the RBS measurements, the samples are coated with 10 nm gold in order to avoid charging under ion irradiation.

# 5 Parameter variations in backside etching of fused silica

## 5.1 The dependency of the etching on the laser fluence

In Fig. 5-1a, the averaged etch depth per laser pulse  $\Delta h$  (left axis) is presented as a function of the applied laser fluence per pulse. A 0.5 mol/l solution of pyrene in toluene is used as absorbing liquid for the incident laser pulses with a wavelength of 248 nm. In addition, the efficiency of etching per laser pulse and fluence ( $E = \Delta h/\Phi$ ; right axis) is shown that gives the etched volume per energy unit. The roughness at smaller fluences measured by WLIM is depicted in Fig. 5-1b.

The experimental threshold fluence  $(\Phi_{th})$  - the smallest fluence at which after 300 pulses a measurable etching occurs - is determined to be 0.33 ±0.03 J/cm<sup>2</sup> which is more than one order of magnitude smaller than for direct laser ablation of fused silica in air (larger than 10 J/cm<sup>2</sup> [65]).  $\Phi_{th}$  of LIBWE processing is not an absolute value and depends strongly on the given experimental parameters, e.g., the pulse number and the spot size of the laser, which will be discussed later (section 7.1). Generally, the behavior of  $\Delta h$  as a function of the laser fluence can be separated into different fluence regions concerning the efficiency of etching and the different surface roughness. The three fluence ranges are: (1) low fluence region, (2) middle fluence region, and (3) high fluences region.

The low fluence region (1) ranges from  $\Phi_{th}$  to 0.60 J/cm<sup>2</sup> and is characterized by a nonlinear increasing of  $\Delta h$  from 0.1 to about 6 nm/pulse (Fig. 5-1a) and a high surface roughness (Fig. 5-1b). The efficiency of etching increases with the fluence, too. The larger roughness is caused by the partially and instable etching of the surface. The partial brightness visible in the SEM image (Fig. 5-2a) is related to an inhomogeneous surface modification. The origin of the modification is amongst others the deposition of decomposition products, which are mainly carbon [16, 103], from the liquid (see subsection 2.4.2). For the middle fluence region (2),  $\Delta h$  increases almost linearly between 0.60 and 1.10 J/cm<sup>2</sup> from 7 to 15 nm/pulse. The efficiency of etching is almost constant and is estimated to be about  $13 \cdot 10^{-7}$  cm<sup>3</sup>/J (Fig. 5-1a). The middle fluence region is characterized by a high quality of etched patterns; the etched pits feature well defined edges and a smooth surface as depicted in the SEM image (Fig. 5-2b). A small roughness in the range of 10 to 20 nm

rms is measured by WLIM (Fig. 5-1b). The linear slope of  $\Delta h$  with the fluence, an etched depth per pulse in the nanometer scale, and the small roughness are characteristic attributes for LIBWE with organic absorbers [8, 14, 15]. In principal, the SEM images of the etched pits at medium fluences (represented by Fig. 5-2b) show minor visible modification preferred at the edges outside the irradiated area, too.



Fig. 5-1: a) Averaged etch depth per laser pulse  $\Delta h$  (left axis) and the efficiency of etching per laser pulse *E* (right axis) as a function of the laser fluence. 300 pulses are applied with a 0.5 mol/l solution of pyrene in toluene as absorbing liquid at  $\lambda = 248$  nm. The dependence of  $\Delta h$  on  $\Phi$  can be separated into the low (1), middle (2), and high (3) fluence regions. b) The absolute roughness of the etched fused silica surface (left axis) and the roughness normalized on the received etch depth after 300 pulses (right axis) for smaller fluences measured by WLIM (data field:  $(11 \cdot 11) \mu m^2$ ). (The lines are used to guide the eyes.)

In the high fluence region (3), the etching is characterized by large values of  $\Delta h$  (up to 150 nm/pulse), an increasing efficiency of etching from 16 to  $35 \cdot 10^{-7} \text{ cm}^3/\text{J}$ , and a high roughness (Fig. 5-1). The last is related to the occurrence of surface features typical for a rapid resolidification after melting (Fig. 5-2c) and is an indication for an ablation-dominated etch mechanism similar to laser ablation in air [65].

Since the roughness in the middle fluence region is small, the etching is determined due to a homogeneous etch mechanism. The constant efficiency in etching and consequently the proportional rise of  $\Delta h$  with  $\Phi$  as well as the small roughness (Fig. 5-1a) matters an etch mechanism that is homogeneous and deterministic over the irradiated area. Furthermore, the small etch depth per pulse and roughness indicates a localized energy deposition in the near surface region of the solid.  $\Delta h$  rises stronger than proportional to  $\Phi$  in the low and high fluence region. This suggests together with the high roughness in both fluence regions that an undetermined and stochastic etch mechanism dominates the etching process. For small fluences, the statistically distributed modification of the surface causes probably an inhomogeneous etching. A similar effect known as incubation takes place for defect-induced materials erosion of transparent solids near the etch threshold [17,



30 µm



Fig. 5-2: SEM images of etch pits in fused silica using 0.5 mol/l solution of pyrene in toluene as liquid absorber for fluences of a)  $0.34 \text{ J/cm}^2$ , b)  $0.94 \text{ J/cm}^2$ , and c)  $1.40 \text{ J/cm}^2$  applying 300, 300, and 30 pulses, respectively.

19, 29, 65, 104]. At high fluences, an ablation-like etch mechanism probably causes the etching. The large roughness and  $\Delta h$  gives evidence for heating a relative thick layer of the material typically for ablation processes [19, 29, 65].

In this work, in particular the low and middle fluence regions are investigated and discussed due to their importance to understand the etch mechanism and the promising attributes of the etching for application (small etched depths per pulse, high quality of etched microstructures).

# 5.2 The influence of the pulse number

Fig. 5-3a to d show SEM images of etch pits after 1, 2, 3, and 10 pulses etched with a laser fluence of 0.99 J/cm<sup>2</sup>. For the 1<sup>st</sup> pulse, probably a deposition of decomposition products takes place that is described by the completely bright area in Fig. 5-3a. The median height of the film is measured by WLIM to be about 3 nm. The 2<sup>nd</sup> laser pulse etches the material but the erosion is inhomogeneous over the irradiated area (Fig. 5-3b). The etched zone in the left part of the area again appears bright in the SEM image whereas other parts inside the spot size have a less



Fig. 5-3: SEM images of etched pits at a fluence of  $\Phi = 0.99 \text{ J/cm}^2$  for a) 1 pulse, b) 2 pulses, c) 3 pulses, d) 10 pulses. The respective depths are: -3 nm, 8 nm, 25 nm, and 130 nm. The negative etch depth for 1 laser pulse indicates the deposits from liquids decomposition. A 0.5 mol/l solution of pyrene in toluene is applied as absorbing liquid at  $\lambda = 248$  nm.

intensive backscattering signal similar to the nonirradiated surface. Thus, the film deposited after the first pulse is removed without an etching of the fused silica and a redeposition of a new layer. The outer bright rim indicates the border of the irradiated area. After 3 and 10 pulses (Fig. 5-3c and d) a homogeneous and smooth etching can be observed.



Fig. 5-4: a) Etch depth (left axis) and averaged etch depth per laser pulse,  $\Delta h$ , (right axis) of fused silica in dependence on the number of incident laser pulses. A 0.5 mol/l solution of pyrene in toluene is applied at  $\lambda$  = 248 nm and different laser fluences. b) Measured absolute surface roughness (left axis) and the roughness normalized on the respective etch depth (right axis) in dependence on the pulse number for 0.99 J/cm<sup>2</sup>. Roughness data are obtained from an area of (11 · 11) µm<sup>2</sup> (WLIM) and (2 · 2) µm<sup>2</sup> (AFM).

Fig. 5-4a (left axis, open symbols) shows the etch depth in dependence on the pulse number for different laser fluences. At  $\Phi = 1.65 \text{ J/cm}^2$ , etching takes place with the first pulse. For  $\Phi = 0.74 \text{ J/cm}^2$  and  $0.99 \text{ J/cm}^2$ , the etching begins with the 7<sup>th</sup> and 2<sup>nd</sup> pulse and the etched depth increases nonlinearly with the number of incident laser pulses. After the pulse number exceeds a fluence-specific quantity, the final depth of the etched pits increases linearly and refers to a constant value of  $\Delta h$ . As a consequence of the observed nonlinear growth of the etch depth, the calculated values of  $\Delta h$  initially increase with the pulse number and saturate at fluence-specific pulse numbers (right axis in Fig. 5-4a, solid symbols). For 1.65, 0.99, and 0.74 J/cm<sup>2</sup>, a constant  $\Delta h$  can be observed at 10, 30, and 300 pulses, respectively. The respective values of  $\Delta h$  after saturation are estimated to about 36, 16, and 10 nm/pulse for 1.65, 0.99, and 0.74 J/cm<sup>2</sup>, respectively.

In Fig. 5-4b, the optically (WLIM) measured roughness in dependence on the pulse number employing  $\Phi = 0.99 \text{ J/cm}^2$  is presented. Initially, a small roughness (below 10 nm) of the etched surface (left axis, open symbols) evolves with raising pulse number but increases up to about 70 nm for N > 100. The respective (short-wavelength) microroughness measured by AFM is below 5 nm rms even after 1000 pulses. By normalizing the roughness with the respectively etched depth, the estimated values (right axis, solid symbols) decrease with the number of pulses. Thus, the large measured values of roughness at high pulse quantity are caused by the waviness of the etched surface. When applying larger numbers of pulses, the fluctuations in the fluence distribution influence the etched surface morphology and consequently the measured roughness noticeable.

#### 5.3 The effect of the spot size of the laser beam

Fig. 5-5 shows  $\Delta h$  of fused silica as a function of the spot size of the laser beam  $A_S$  for different fluences. The pulse quantity is fixed (N=300) and a 0.5 mol/l solution of pyrene in toluene is employed.  $\Delta h$  first rises with  $A_S$  and shows saturation after exceeding a fluence-specific spot size. For 1.10, 0.90, and 0.65 J/cm<sup>2</sup>,  $A_S$  at  $\Delta h$  saturation decreases from 40000 to 22500 and 6400 µm<sup>2</sup>, respectively.

The observed etch behavior is opposite to the size dependence at the ablation with ns laser pulses in air where  $\Delta h$  increases with decreasing spot size [105, 106]. At ablation, the reasons of the enhanced ablation depth per pulse with reduced spot

size are the interactions of the laser pulse with the ablation plasma or the evolving surface microstructure. In the case of LIBWE, no plasma shielding takes place due to the opposite plume propagation with respect to the incidence direction of the laser beam. Reflection or scattering on roughness or ripples of the surface cannot influence the etching significantly because the difference in refractive index between the solid and the liquid is very small (*Table A 1, Table A 2*).

The influence of the forces released at the bubble collapse increase with increasing laser spot size [53, 55] but can be ruled out due to the suggested etch mechanism (see section 3.3). The laser-induced jump in pressure in the initial stage of liquids heating is independent on the irradiated area concerning (2-18). A significant influence of the spot size on heat diffusion out of the heated solid volume as proposed by Wang et al. [107] can be ruled out, too. The heat diffusion length in toluene and fused silica after  $t = \tau_p$  can be approximated with (2-7) to about 100 nm and 300 nm, respectively, which is small in comparison with the applied spot sizes.

In Ref. [108], the influence of the laser spot size on the etching is explained by the modification of the surface due to the products from liquid decomposition. The degree of the surface modification depends probably on the occurrence of vapor bubbles that contain the decomposition products. The size and the lifetime of the bubble as a function of the laser pulse energy and consequently the spot size [53,



Fig. 5-5: Average etch depth per laser pulse,  $\Delta h$ , of fused silica as a function of the spot size of the laser beam for different laser fluences after 300 pulses. A 0.5 mol/l solution of pyrene in toluene is applied as absorbing liquid at  $\lambda$  = 248 nm.

54] may affect the degree of modification and the etch process itself. The effect of surface modification on the etching will be discussed in chapter 7 more detailed.

If microstructures with different sizes but a constant depth have to be written into surfaces, different numbers of pulses have to be applied for etching. Both, the spot size as well as the pulse number affect  $\Delta h$  for fixed laser fluences in a nonlinear manner and have to be taken into account by adjusting the processing parameters.

## 5.4 The effect of the pulse repetition rate

The laser-induced processes at the solid-liquid interface like the formation of bubbles are slow in comparison with the laser pulse duration. However, the time interval between two subsequent pulses may affect the etching. Fig. 5-6 shows  $\Delta h$  as a function of  $f_p$  between 1 and 100 Hz (the maximal repetition rate of the laser system) for different laser fluences. The estimated values of  $\Delta h$  in dependence on  $f_p$ are not constant.  $\Delta h$  first increases, reaches a maximum at 40 Hz, and then decreases continuously. The occurrence of the maximum becomes more apparent with increasing fluence.

The time interval between two pulses at 100 Hz is 10 ms and the lifetime of a bubble at similar conditions was estimated to less than 500  $\mu$ s [83, 109]. Thus, the following laser pulse cannot interact with the vapor bubble. Even repetition rates up



Fig. 5-6: Etch depth per laser pulse  $\Delta h$  of fused silica as a function of the pulse repetition rate for different laser fluences and after 300 pulses. A 0.5 mol/l solution of pyrene in toluene is applied as absorbing liquid at  $\lambda$  = 248 nm. (The lines are used to guide the eye.)

to about 2 kHz can be applied without risk to hit a bubble from the former laser pulse. Moreover, the laser fluence is estimated as constant for the different repetition rates due to the feedback control of the pulse energy by the laser. Consequently, bubble dynamics [83, 85] may not affect the etching at the investigated repetition rates. Latent processes like the decomposition of the liquid and the deposition of the decomposition products can change the chemical and physical properties of the solid-liquid interface. The duration of these processes will be longer than the bubble lifetime and can probably affect  $\Delta h$  with respect to the pulse repetition rate.

## 5.5 The influence of the absorbing liquid

#### 5.5.1 Variation of the pyrene concentration

To investigate the influence of the absorbance of the liquid on etching, the concentration of pyrene in the absorbing liquid (toluene is the solvent) is varied. The measured linear absorption coefficients are given in *Table 5.1*. The absorbance of the liquid increases with the pyrene content up to 0.4 mol/l and remains almost constant for 0.5 mol/l and larger concentrations since the solute saturates.

The graph in Fig. 5-7a presents  $\Delta h$  as a function of the laser fluence for different concentrations of solved pyrene in toluene and the pure solvent (0.0 mol/l). In principle, the behavior of  $\Delta h$  and the respective *E* are similar to the results in section 5.1 concerning the separation into the three fluence regions (Fig. 5-7b). However, the threshold fluences and the efficiency in etching depend on the dye concentration and consequently the absorption coefficient of the liquid  $\alpha^L$ . Otherwise, the transition from low to middle fluence region is not significantly affected by the content of pyrene in the liquid.

Pyrene concentration (mol/l)	$\Phi_{th}$ (J/cm <sup>2</sup> )	$\alpha^{L}$ (10 <sup>3</sup> cm <sup>-1</sup> )
0.0	0.45	1.7
0.05	0.40	2.8
0.1	0.40	3.7
0.2	0.37	5.9
0.4	0.33	10.6
0.5	0.33	11.0

Table 5.1: Measured linear absorption coefficient ( $\alpha^L$ ) for  $\lambda = 248$  nm and estimated threshold fluences of toluene solutions containing different pyrene concentrations.

The pyrene concentration distinctly affects the etching up to 0.4 mol/l (Fig. 5-7). In particular, the threshold fluences drop (*Table 5.1*) and the efficiency of etching in the middle fluence region increases (Fig. 5-7b) with increasing pyrene concentration. For larger concentrations, the behavior of  $\Delta h$  and *E* differs not significantly. Otherwise, in the case of the pure solvent, the efficiency of etching as a function of the laser fluence differs from that of the solutions of pyrene. *E* increases in the low fluence region and decreases for fluences in the middle fluence region.



Fig. 5-7: a) Averaged etch depth per laser pulse,  $\Delta h$ , and b) the efficiency of etching per laser pulse as a function of the laser fluence. 300 pulses are applied at  $\lambda = 248$  nm for each data point. Different solutions of pyrene in toluene are employed as absorbing liquid.

Concerning the proposed etch mechanism, the absorption of the incident laser pulse by the liquid on the back surface is the basic process for LIBWE (section 3.3). A larger absorbance causes a smaller laser-heated liquid volume that consequently results in larger temperatures at solid-liquid interface (according to the calorimetric solution of the heat equation (2-12)). Thus, the ratio of the absorption coefficients for the different concentrations of pyrene must be equal to the ratio of threshold fluences considering a constant critical temperature for etching. But this has not been found in the experiment (*Table 5.1*). In particular, the 6.5 times larger absorption coefficient of a 0.5 mol/l solution of pyrene in toluene in comparison to the pure solvent results in an only 1.4 times reduced threshold fluence. Thus, the etching process seems not directly related with the linear absorption of the liquid or with the content of pyrene. Furthermore, the addition of pyrene does not basically affect the etch mechanism because of the similar etch behavior ( $\Delta h$  and E) of the solutions of pyrene in toluene in toluene in toluene in the pure solvent.

#### 5.5.2 The effect of the solvent

Beside the optical properties, e.g., the absorption coefficient, other physical properties of the liquid may have an influence on LIBWE. For instance, the laserinduced temperatures at the interface depend on the heat capacity and the thermal diffusion length (section 3.3). Additionally, the mass density and the sound velocity determine the pressure impact of the solid surface during and after laser irradiation (subsection 2.4.1). The decomposition of the molecules due to intensive laser irradiation differs strongly between different kinds of organic solvents [59].

The liquids, which are used for LIBWE, can be grouped into four classes: (i) pure organic solvents, (ii) organic dyes solved in organic solvents, (iii) aqueous solutions of organic dyes, and (iv) aqueous inorganic solutions. The classes (i) and (ii)

Absorbing liquids	$\alpha^L$ (10 <sup>3</sup> cm <sup>-1</sup> )	$\Phi_{th}$ (J/cm <sup>2</sup> )
Xylene (C <sub>8</sub> H <sub>10</sub> )	1.7	0.48
Acethylacetone ( $C_5H_8O_2$ )	53.0	0.45
0.4 mol/l pyrene in acetone	7.8 [8]	0.46
0.5  mol/l pyrene in chlorobenzene (C6H5Cl)	11.0	0.34
$0.5 \text{ mol/l pyrene in dichlorobenzene } (C_6H_4Cl_2)$	9.0	0.34
0.5 mol/l pyrene in fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	9.8	0.34

Table 5.2: Measured linear absorption coefficients ( $\alpha^{L}$ ) for  $\lambda = 248$  nm and estimated threshold fluences of the different absorbing liquids.

can contain halogenated and non-halogenated solvents to investigate the influence of a chemical affected etch mechanism on LIBWE. The groups (iii) and (iv) are not subject of this work but are studied by Ding et al. [71, 110] and Shafeev et al. [111-113], respectively.

#### Non-halogenated solvents

In the literature, a multitude of non-halogenated organic solvents and solutions were investigated [8, 15, 74, 83, 103, 114]. In Fig. 5-8 the etch depth per pulse as a function of the laser fluence at  $\lambda$  = 248 nm is shown for selected non-halogenated liquids of the classes (i) and (ii). The aliphatic ketone acethylacetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>) presents a polar solvent for dissolving a broad range of organic and inorganic dyes or salts which is interesting for future work on LIBWE processing. Xylene (C<sub>8</sub>H<sub>10</sub>) as another benzene derivate is used. Additionally to the pure organic solvents, 0.4 mol/l solution of pyrene in acetone is employed because it was the liquid used first to demonstrate LIBWE of fused silica with high surface quality [8, 102]. The magnitude of  $\alpha^{L}$  differs strongly between the solvents and the solution and covers a range of about 30 (*Table 5.2*).

All used liquids feature roughly the same characteristic in  $\Delta h$  as a function of  $\Phi$  like pyrene in toluene solutions or pure toluene (subsection 5.5.1) despite the strongly



Fig. 5-8: Etch depth per laser pulse  $\Delta h$  (left axis) and efficiency of etching *E* (right axis) as a function of the laser fluence. 300 laser pulses are applied at  $\lambda = 248$  nm for each data point. Acethylacetone, xylene, and a 0.4 mol/l solution of pyrene in acetone are employed as absorbing liquid.

different molecule structures, absorption coefficients, and the addition of pyrene. The three liquids (acethylacetone, xylene, and 0.4 mol/l solution of pyrene in acetone) have a similar small etching threshold at about 0.45 J/cm<sup>2</sup> like pure toluene (*Table 5.1*). This confirms the findings in subsection 5.5.1 that the etching process is not directly related with the linear absorption of the liquid. The efficiency of etching reveals the differences between the liquids; acethylacetone offers an only small middle fluence region (about 0.5 to 0.8 J/cm<sup>2</sup>) whereas the separation into the different fluence regions for xylene and 0.4 mol/l solution of pyrene in acetone is similar for both liquids (about 0.7 to 1.2 J/cm<sup>2</sup>).

#### Halogenated liquids

To investigate the effect of halogenated liquids on the etching process, molecules with similar chemical structure and optical properties are useful. Thus, different benzene derivates containing one and two substituted species are used as solvent: fluorobenzene ( $C_6H_5F$ ), chlorobenzene ( $C_6H_5Cl$ ), and dichlorobenzene ( $C_6H_4Cl_2$ ). To ensure a similar linear absorption coefficient, pyrene is dissolved in a concentration of 0.5 mol/l.

Fig. 5-9a shows the dependence of  $\Delta h$  and *E* on the laser fluence for the halogenated liquids. In principle, the etching characteristic ( $\Delta h$  and *E*) of fused silica at  $\lambda = 248$  nm by employing the halogenated solvents can be separated into the different fluence regions similar to the non-halogenated liquids. The determined etch threshold of about 0.34 J/cm<sup>2</sup> does not significantly deviate between the halogenated or the non-halogenated aromatic solutions.

Similar to the etching with toluene (Fig. 5-1a), a strong nonlinear increase and a linear rise of  $\Delta h$  is found in the low fluence region (smaller than 0.60 J/cm<sup>2</sup>) and in the middle fluence region (about 0.60 to 1.20 J/cm<sup>2</sup>), respectively (Fig. 5-9a). The small roughness and the almost constant efficiency of etching as known from pyrene in toluene solutions in the middle fluence region are observed for the halogenated solvents, too (Fig. 5-9a and b). Thus, the mechanism that dominates the etching in this fluence region is similar for halogenated and non-halogenated solvents. The high fluence region with its typical ablation-like topographic characteristics, large  $\Delta h$  and roughness, and growing *E* is not shown in Fig. 5-9a.

However, essential differences are found for the halogenated aromatic liquids in

comparison with toluene: (i) a homogeneous and smooth etching with very small  $\Delta h$  (about 0.1 nm/pulse) for small laser fluences (Fig. 5-9a and b), (ii) a sudden increase of  $\Delta h$  at a certain laser fluence, and (iii) a usually smaller value of  $\Delta h$  in the whole investigated fluence range. With employing fluorinated benzene in comparison to chlorinated solvents smaller  $\Delta h$ , *E*, and roughness have been found.

Fig. 5-10 shows an etch pit with an averaged depth of about 7 nm fabricated with



Fig. 5-9: a) Etch depth per laser pulse  $\Delta h$  (left axis) and efficiency of etching *E* (right axis) as a function of the laser fluence. 300 laser pulses are applied at  $\lambda = 248$  nm for each data point. 0.5 mol/l solutions of pyrene in different halogenated solvents are employed as absorbing liquid. b) The absolute roughness (rms) of the etched fused silica surface after 300 pulses for smaller fluences measured by WLIM (data field:  $(11 \cdot 11) \mu m^2$ ).

300 pulses at a laser fluence of 0.36 J/cm<sup>2</sup> using a 0.5 mol/l solution of pyrene in fluorobenzene. The small holes inside the otherwise homogeneous etched area let infer a preferred etching at surface defects. Outside the laser-irradiated area, a slight etching of the adjacent areas has been observed. The mentioned attributes are characteristic for the halogenated solvents but are not observed with non-halogenated hydrocarbons.

Changed decomposition products appear when halogenated benzene derivates are applied instead of toluene [59, 115]. Additionally to the different hydrocarbon and carbon products at toluene decomposition (section 6.3), halogenated compounds as well as halogen radicals are produced in the case of halogenated benzenes [59, 115]. The estimated  $\Delta h$  in the Angstrom range at fluences less than 0.50 J/cm<sup>2</sup> as well as a homogeneously etched surface (Fig. 5-10) are typical for a laser-induced chemical corrosion of fused silica in chlorine or fluorine atmosphere ([116] and Refs. cited in [17]). Concerning the respective coefficients of diffusion for chlorine and fluorine in fused silica at large temperatures (e.g.  $5 \cdot 10^{-9} \text{ cm}^2/\text{s}$  at 2000°C [117]) their length of diffusion during the pulse duration can be approximated to about 0.2 nm that equals the measured value of  $\Delta h$  at small fluences sufficiently. With the presence of halogen radicals due to photolysis a chemical reaction between the radicals and the fused silica surface may result in material erosion [118]. Because the used halogenated solvents are inert at room conditions, both the temporary formation of halogen compounds near the interface and the short-term laser-induced temperatures can lead to the observed etch effects. This chemical etch mechanism is obviously present at large fluences too but has no significant effect



Fig. 5-10: WLIM-recorded morphology of an etch pit fabricated with 300 pulses at 0.36 J/cm<sup>2</sup> employing a 0.5 mol/l solution of pyrene in fluorobenzene at  $\lambda = 248$  nm. Additional to the small etch depth small holes in the etched surface and a shallow etched surrounding area are visible.

to the overall value of the etch depth per laser pulse.

A chemical-assisted etching due to the generation of radicals seems possible in the case of non-halogenated solvents, too. In particular, the main products of the one-step photolysis of toluene are phenyl and hydrogen radicals [52, 58]. It is known from the literature that hydrogen radicals can be trapped by the silicon dangling bonds [119] (also denoted as oxygen vacancies or E' center defects; see subsection 2.2.2) preferred at the surface of fused silica. To form the volatile SiH<sub>4</sub>, the silica tetrahedron has to be completely reduced by hydrogen. Another possible mechanism is the formation of silicic acids (SiO<sub>2</sub> · x H<sub>2</sub>O) which can be probably dissolved by the absorbing liquid. In any case the concentration of both defects and radicals must be sufficiently large.

The temperature of the interface region of fused silica and a 0.5 mol/l solution of pyrene in toluene (as another non-halogenated liquids) can be approximated calorimetrically with (3-2) (section 3.3) and the respective data (Table 5.1, Table A 1, and Table A 2). An increase of the temperature of about 1470 K is calculated for a fluence of 1.00 J/cm<sup>2</sup>. The coefficient of diffusion for molecular hydrogen in fused silica is about 10<sup>-6</sup> cm<sup>2</sup>/s at 1500°C [120]. Thus, the length of diffusion during the time duration of the laser pulse can be approximated to about 3 nm. This value is smaller than the observed respective etch depth per pulse ( $\Delta h = 12 \text{ nm/pulse}$ ) if the length of diffusion of the hydrogen radicals is adequate to the achieved value of  $\Delta h$ . Furthermore, to guarantee a homogeneous etching of the surface, almost every silica tetrahedron of the material layer to be etched must have at least one oxygen vacancy as defect that can trap the hydrogen radicals. This chemical-assisted etch mechanism due to hydrogen radicals can be discussed together with SiO<sub>2</sub> but seems rather speculative in case of the non-halogenated solvents and cannot be applied on materials with different chemical structure (e.g., MgF<sub>2</sub> or sapphire; section 5.7) or absorbing liquids without a hydrogen content (e.g.,  $C_2Cl_4$  [68]).

## 5.5.3 Summary of liquid variation

By employing different absorbing liquids, the etch depth per pulse after 300 laser pulses ranges from 0.1 to 20 nm/pulse whereas a surface roughness of below 10 nm rms can be achieved. The similar characteristics of  $\Delta h$ , *E*, and roughness as a function of the laser fluence for the investigated liquids suggest similar etch mechanisms that dominate the backside etching in the defined fluence regions. Furthermore, the threshold fluences of etching are almost on the similar order for the applied liquids. Since the liquids/solvents possess similar physical properties (*Table A 2, Table A 3*) but strongly different coefficients of linear absorption (*Table 5.1, Table 5.2*), the etching process cannot be explained by the mechanism as proposed in the literature (section 3.3) that the laser pulse initially heats the liquid and the hot liquid thereafter melts the solid. A chemical-assisted etching of fused silica direct by the radicals seems possible by employing halogenated solvents but the etching effect due to the halogen radicals is rather small. Consequently, other mechanisms must dominate the etching process at LIBWE.

## 5.6 LIBWE at different laser wavelengths

The LIBWE process is usually investigated for nanosecond excimer lasers [8, 13, 16, 68, 71-74, 77-82]. Applying different laser gas media, wavelengths from 193 nm to 351 nm can be used with similar pulse duration (25 ns) and beam homogeneity to study the effect of the photon energy on the etching. The short wavelengths of the ArF and KrF lasers possess large photon energies perfectly suited for the absorption in organic solutions and to etch UV transparent materials like fused silica and optical crystals [8, 11, 68]. The XeF wavelength can extend LIBWE to materials with cut-off wavelengths larger than 300 nm, e.g., technical glasses [13].



Fig. 5-11: Etch depth per laser pulse  $\Delta h$  (open symbols, left axis) and efficiency of etching *E* (solid symbols, right axis) as a function of the laser fluence for different laser wavelengths. 300 pulses are applied for each data point with a 0.5 mol/l solution of pyrene in toluene as absorbing liquid.

The etch depth per pulse and the efficiency of etching are shown in Fig. 5-11 as a function of the laser fluence at 193 nm (ArF), 248 nm (KrF), and 351 nm (XeF). The characteristic of  $\Delta h$  with the fluence and the respective efficiencies for  $\lambda$  = 351 nm and  $\lambda$  = 193 nm are similar to that described in section 5.1 for  $\lambda$  = 248 nm. The wavelength of the laser pulses distinctly affects the etching: the threshold fluences drop (*Table 5.3*) whereas  $\Delta h$  and *E* (in the middle fluence region) increase with decreasing wavelength. As middle fluence region, fluences in the range of 0.28 to 0.40 J/cm<sup>2</sup>, 0.60 to 1.10 J/cm<sup>2</sup>, and 0.90 to 1.80 J/cm<sup>2</sup> can be determined from the constant efficiency of etching for 193 nm, 248 nm, and 351 nm, respectively.

The very small threshold and the large  $\Delta h$  and *E* at 193 nm are the result of the large absorption of the liquid at this wavelength in comparison to the longer wavelengths (Table 5.3). Otherwise, similar to subsections 5.5.1 and 5.5.2 the 7.3 and 270 times larger absorption coefficient at  $\lambda$  = 193 nm in comparison with  $\lambda$  = 248 and 351 nm results in only 2.4 and 3.3 times reduced threshold fluence, respectively, that disagree with the proposed etch mechanism for LIBWE (section 3.3). On the other side, the occurrence of decomposition of the absorbing liquid (sections 5.1 and 5.5) is an indication for photon-induced processes in the liquid (subsection 2.4.2). Thus, the energy of the photons must have an influence on the photolysis of the liquid. If a chemical etch mechanism dominates LIBWE, the number of radicals to initiate the etching should be equal for the different laser wavelengths. The generated number of species per time within the volume of the liquid at the threshold fluence can be estimated with (2-21) for the different laser wavelengths. For approximation, the quantum yield of the photochemical dissociation is similar and no diffusion or recombination of the radicals occurs. According to (2-21), the threshold fluence for  $\lambda$  = 193 nm in comparison with  $\lambda$  = 248 and 351 nm must be reduced 5.7 and 146 times but in the experiment (Table 5.3) a reduction of only 2.4 and 3.3 times have been found, respectively. Thus, a direct photochemical etching

Table 5.3: Measured linear absorption coefficients ( $\alpha^{L}$ ) of 0.5 mol/l solution of pyrene in toluene and  $\Phi_{th}$  at different excimer laser wavelengths.

of fused silica due to free radicals by employing non-halogenated solvents can be disregarded as mechanism that dominates the etching. This is additionally confirmed by the discussion in subsection 5.5.2.

## 5.7 The variation of the transparent material

The longer wavelength of the XeF excimer laser ( $\lambda = 351$  nm) is used in order to extend LIBWE to technical glasses. Four glass samples: (i) Pyrex, (ii) 7059 (both Corning Inc.), (iii) D263, and (iv) BK7 (both Schott Group) are included in this study. In Fig. 5-12a, the average etched depth per pulse is shown as a function of the laser fluence for technical glasses. A 0.5 mol/l solution of pyrene in toluene is employed as absorbing liquid. The characteristic of  $\Delta h$  for the technical glasses is similar: it grows continuously with increasing laser fluence. If the efficiency of etching (not presented in the figure) and the surface roughness [13] are considered, the middle fluence region ranges for all glasses from 0.9 to 1.6 J/cm<sup>2</sup>. The surface quality in etching of the technical glasses is as high as that of fused silica [13, 121-123]. Compared with fused silica (Fig. 5-11), the threshold fluences are larger and  $\Delta h$  is generally smaller.  $T_g$  of fused silica is significantly larger than the temperatures of glass transition of the technical glasses while the other thermal materials properties, e.g.,  $c_p$ ,  $\kappa$ , or  $\rho$  are almost similar (*Table A 1* and *Table A 4*). Thus, the temperature of glass transition appears not as the critical temperature for the LIBWE process. The reason for the differences in  $\Phi_{th}$  and  $\Delta h$  is probably the chemical composition of the technical glasses but a prediction of the influence of the additives on the etching cannot be given yet.

Fig. 5-12b presents  $\Delta h$  as a function of the laser fluence at  $\lambda = 248$  nm of the crystalline materials quartz, MgF<sub>2</sub>, CaF<sub>2</sub>, and sapphire. A 0.5 mol/l solution of pyrene in toluene is employed as absorbing liquid. The threshold fluences are determined to about 0.34, 0.37, 0.66, and 0.71 J/cm<sup>2</sup> for CaF<sub>2</sub>, quartz, MgF<sub>2</sub>, and sapphire, respectively. The quartz features the same chemical structure as fused silica and the etching results in similar quality (see SEM image in Fig. 5-13a) and  $\Delta h$ . MgF<sub>2</sub> shows beside smaller etch rates also larger surface roughness, which is illustrated in Fig. 5-13b. The visible patterns on the etched surface are regular and let infer an influence of the crystalline microstructure onto the etching. For sapphire and for fluences up to 1.30 J/cm<sup>2</sup>,  $\Delta h$  grows only little and is in the range of 1 nm per pulse.

With exceeding a fluence of 1.30 J/cm<sup>2</sup>,  $\Delta h$  increases steeply. At  $\Phi > 4.00$  J/cm<sup>2</sup>, the front side of the sample is ablated [19]. The morphology of the etched surface indicates a materials melting and resolidification process; the center of the etch pit is even and smooth whereas a rough and (relative to the central plane) elevated rim surrounds it (Fig. 5-13c). The etching of CaF<sub>2</sub> is characterized by a smaller threshold and larger  $\Delta h$  in comparison to the other crystals (Fig. 5-12b). The etch qual-



Fig. 5-12: Averaged etch depth per laser pulse,  $\Delta h$ , of a) the investigated glasses at  $\lambda = 351$  nm and b) the crystalline materials at  $\lambda = 248$  nm. 300 pulses are applied with a 0.5 mol/l solution of pyrene in toluene.

ity is very poor (Fig. 5-13d). The surface morphology is characterized by a granular and clod-sized figure. Furthermore, the edges of the etch pit are not well defined.

The separation of the behavior of  $\Delta h$  as a function of  $\Phi$  into the three fluence regions with considering the efficiency of etching (not presented in the figure) is possible for the crystalline materials except CaF<sub>2</sub>. While the middle fluence region for quartz, MgF<sub>2</sub>, and sapphire ranges from 0.75 to 1.50 J/cm<sup>2</sup>, 1.30 to 2.00 J/cm<sup>2</sup>, and 0.90 to 1.30 J/cm<sup>2</sup>, respectively, for CaF<sub>2</sub> no middle fluence region seems to exist. The efficiency of etching grows continuously with the fluence and the low fluence region merges directly into the high fluence region. This suggests the influence of an unknown effect on the etch mechanism in the case of CaF<sub>2</sub>.

The surface morphology of etched sapphire,  $CaF_2$ , and  $MgF_2$  in (Fig. 5-13) gives evidence for a quenching process in combination with thermal-induced stress. During laser-induced materials heating, the surface melts and is removed partly. Due to the large thermal conductivity of the crystals (*Table A 4*), the heat is very fast conducted into the bulk of the material, especially at the edge of the irradiated area. Contrary to the center of the groove, the heat transfer can occur here to the



Fig. 5-13: SEM images of different crystalline materials: a) quartz ( $\Phi = 1.00 \text{ J/cm}^2$ , 300 pulses); b) MgF<sub>2</sub> ( $\Phi = 1.35 \text{ J/cm}^2$ , 100 pulses); c) sapphire ( $\Phi = 1.20 \text{ J/cm}^2$ , 1000 pulses), d) CaF<sub>2</sub> ( $\Phi = 0.80 \text{ J/cm}^2$ , 500 pulses), etched with a 0.5 mol/l solution of pyrene in toluene.

surrounding materials volume, too, and is not limited due to the almost onedimensional heat flow in the center. Thus, the quenching process must be much stronger at the edge than in the center of the etch pit.

Because the materials properties of the technical glasses do not differ significantly, only the crystalline materials are compared with fused silica (*Table A 1, Table A 4*). To discuss the influence of the kind of material on the etching, the heat flux inside the solid material and consequently the maximal surface temperature has to be approximated. The solution of the one-dimensional heat equation concerning an infinite surface absorbance (2-10) can be applied in a good approximation with concerning the equations (2-7) and (2-2). Considering  $T_C = T_M$  of the materials, the relation between the threshold fluence and the materials properties is:

$$\Phi \propto \sqrt{\pi \kappa \varrho} c_p \tau_p \Delta T_C \tag{5-1}$$

(5-1) presents a relation for the one-dimensional heat flux during the duration of the laser pulse from the surface to the bulk of the material. Consequently, the larger the heat flux the larger the laser fluence necessary to reach  $T_c$ .

In Fig. 5-14 the experimentally determined threshold fluences of the crystalline materials and fused silica are shown in dependence on the heat flux. Concerning (5-1) and the respective materials properties (*Table A 1* and *Table A 4*) the heat



Fig. 5-14: Experimental threshold fluence (symbols) of fused silica, quartz,  $MgF_2$ ,  $CaF_2$ , and sapphire in dependence on the heat flux from surface to the bulk of material concerning (5-1). The calculated heat fluxes are normalized to that of fused silica. The line presents a linear fit of experimental data.

fluxes are calculated and normalized to the value of fused silica. The included linear fit satisfyingly indicates the tendency of the experimental data. Thus, the materials properties affect the etching process for the investigated materials, in particular for the threshold fluences. But (5-1) gives no prediction about the effect of other material parameters such as the coefficient of thermal expansion. Additionally, the structural properties of the material, e.g., the kind of crystal lattice, can have an influence on the etching.

In summary, the variation of the kind of material indicates the influence of the materials properties  $\kappa$ ,  $\rho$ , and  $c_p$  on the thermal etching process. In particular, materials with small thermal conductivity offer smaller  $\Phi_{th}$  and better surface quality. The surface morphology of the crystals sapphire, CaF<sub>2</sub>, and MgF<sub>2</sub> gives evidence for a quenching effect due to rapid cooling as a result of the fast heat transfer into the bulk material that adversely affects the etch quality. The discrepancy between  $\Phi_{th}$ and  $T_g$  of the technical glasses and fused silica as well as the almost identical etch behavior between fused silica and quartz let conclude that softening of the vitreous samples plays no significant role in the etch mechanism.

# 6 Analytical investigations at LIBWE

## 6.1 Analysis of the etched fused silica surface

In this section, the influence of the LIBWE process upon the chemical and structural properties of the surface respective the modified layer is investigated. The properties of the surface after the etching process are analyzed with SEM, AFM, Raman spectroscopy, XPS, and RBS/channeling. The respective sample preparation for the surface analytics is described in detail in 4.4.3.

#### 6.1.1 Characterization with SEM and AFM

A distinct modification of the surface can be recognized from SEM images of etched pits in fused silica (Fig. 5-2 and Fig. 5-3). The deposition of products from liquids photolysis is suggested as the origin of visible surface alterations. In Fig. 6-1 a closer view onto the surface of fused silica etched with a fluence of 0.75 J/cm<sup>2</sup> (a) and 0.35 J/cm<sup>2</sup> (b) is presented. The etch pits ( $A_S = (3 \cdot 3) \text{ mm}^2$ ) are fabricated with 50 pulses at  $\lambda = 248 \text{ nm}$  and a 0.5 mol/l solution of pyrene in toluene. The images are



Fig. 6-1 a) and b): SEM images of fused silica surfaces etched with a fluence of a)  $0.75 \text{ J/cm}^2$  and b)  $0.35 \text{ J/cm}^2$  each with 50 pulses at  $\lambda = 248 \text{ nm}$  and 0.5 mol/l solution of pyrene in toluene. The samples are analyzed without cleaning. c) and d) AFM images of the sample etched with  $0.75 \text{ J/cm}^2$  before (c) and after (d) cleaning procedure.

recorded directly after the etching procedure without cleaning of the sample. The roughness (rms) is measured by AFM from an area of  $(2 \cdot 2) \mu m^2$  to about 8.5 ±0.8 nm and 52.3 ±7.9 nm for the etching with 0.75 J/cm<sup>2</sup> and 0.35 J/cm<sup>2</sup>, respectively. The respective depth of the etch pits are 730 nm and 50 nm.

At  $\Phi = 0.75 \text{ J/cm}^2$  (Fig. 6-1a), which corresponds to the etching process in the middle fluence region, the surface is altered only minimal in comparison with etching in the low fluence region near the threshold fluence ( $\Phi = 0.35 \text{ J/cm}^2$ , Fig. 6-1b). Generally, the surfaces etched with fluences of the middle fluence region reveal relatively smooth with considering the SEM images (Fig. 5-2b, Fig. 5-3, and Fig. 6-1a). However, the AFM image in Fig. 6-1c shows a microroughness, which is not visible in the SEM image due to the much less resolution of SEM compared to AFM (4.3.1 and 4.3.3). Small features with medium diameter in the range of 20 to 50 nm dominate the roughening of the surface. After cleaning the sample with a gentle and selective etching process employing microwave-stimulated oxygen plasma (subsection 4.4.2), the roughness is distinctly reduced. From the AFM image in Fig. 6-1d, a roughness of 0.9 ±0.1 nm is obtained which is only little larger than the roughness of an unprocessed sample of about 0.3 nm.

If the samples are cleaned only ultrasonically in a bath of acetone, the observed modification of the surface remains visible as brown or black coloring of the processed area. After wiping the surface with a soft tissue, the coloring can be much reduced in particular for the low fluences but keeps almost constant for middle fluences. Due to the cleaning procedure with the oxygen plasma, the visible surface alteration can be generally removed and the etched areas become transparent. Consequently, LIBWE generates a distinct modification of the surface within the processed area and at the edges. This layer offers a good adherence to the bulk material in particular at middle fluences and causes probably the measured microroughness in the range of tens of nanometers. The process of surface modification can be observed for the technical glasses [13] as well as for the crystals (Fig. 5-13) and is probably a process-inherent effect.

#### 6.1.2 Investigations with Raman spectroscopy and XPS

In Fig. 6-2 Raman spectra of fused silica surfaces etched with 50 pulses at  $\Phi$  = 0.60 and 1.20 J/cm<sup>2</sup>,  $A_S$  = (100 · 100) µm<sup>2</sup>, and a 0.5 mol/l solution of pyrene in toluene are presented. The samples are cleaned only ultrasonically. The Raman spectrum



Fig. 6-2: Raman spectra of fused silica surface etched at a low fluence (lower curve;  $\Phi = 0.60 \text{ J/cm}^2$ ) and a middle fluence (upper curve;  $\Phi = 1.20 \text{ J/cm}^2$ ) with a 0.5 mol/l solution of pyrene in toluene.

of the etch pit at  $\Phi = 0.60 \text{ J/cm}^2$  shows a double-peaked structure superimposed on the broad photoluminescence background. The peak at about 1595 cm<sup>-1</sup> is related to the *G* line of graphite ("graphite mode") and the maximum at about 1360 cm<sup>-1</sup> stands for the *D* line ("disorder mode"). The recorded Raman spectrum is characteristic for disordered carbon [57, 124] with small regions with graphitic order [124] due to the characteristic difference between the peak height and the peak width of *D* and *G* line. This spectrum is characteristic for amorphous carbon [124]. For the low fluence region (represented by  $\Phi = 0.60 \text{ J/cm}^2$ ) the intensity of the Raman peaks - correlating with the amount of material detected - is enhanced in comparison to the middle fluence region (represented by  $\Phi = 1.20 \text{ J/cm}^2$ ). Here, only weak or no carbon signal can be detected. A similar notice was made by Kopitkovas et al. [103].

Fig. 6-3 illustrates the Si 2p, C 1s, and O 1s core level XPS spectra of a fused silica surface processed with 50 pulses at 1.00 J/cm<sup>2</sup> and a 0.5 mol/l solution of pyrene in toluene. The XPS measurements are affected by a shift of the peaks of about 3 eV resulting from surface charging. The remaining error in peak fitting is 0.26%, 1.12%, and 1.53% for Si 2p, C 1s, and O 1s, respectively. The XPS study shows a distinct contamination of the surface by decomposition products of the used liquid.

An estimation of the chemical composition of the analyzing volume gives atomic percentages for Si:0:C of about 24%:31%:45%.

The multitude of components, which is necessary to obtain a fit result with a minimum error value, is summarized in *Table 6.1*. Several peaks are identified in good agreement with XPS studies of oxygen doped SiC films [125]. The XPS results show that the surface modification is caused not alone by carbon deposits (graphite peak, a-C) but also by an incorporation of carbon products into the fused silica surface due to the existence of the silicon carbide (Si-C) and silicon-oxy-carbide



Fig. 6-3: Si 2p, C 1s, and O1s core level spectra of fused silica etched with  $\Phi = 1.00 \text{ J/cm}^2$ , 100 pulses and a 0.5 mol/l solution of pyrene in toluene as absorbing liquid at  $\lambda = 248 \text{ nm}$ .
Peak	Si 2p		C 1s		0 1s	
	BE (eV)	AP (%)	BE (eV)	AP (%)	BE (eV)	AP (%)
Si-Si	98.4	1.7				
Si-C	101.5	24.3	283.5	42.4		
Si-O-C	103.0	32.4			531.2	6.0
SiO <sub>2</sub>	103.9	38.5			531.8	94.0
a-C (graphite)			284.8	48.6		
>C=0			287.7	1.8		
C-00-			288.7	7.0		

Table 6.1: XPS data of fused silica etched with 100 pulses at 1.00 J/cm<sup>2</sup> and 0.5 mol/l solution of pyrene in toluene as absorbing liquid after fitting procedure for Si 2p, C 1s, and O 1s core levels. BE and AP stands for binding energy and atomic percentage, respectively.

(Si-O-C) peaks in the spectra.

#### 6.1.3 Rutherford Backscattering

Due to the demand of RBS for crystalline samples, quartz is used instead of fused silica. Because the  $\Delta h$  and the surface quality are similar for quartz and fused silica (section 5.5.3), a comparison of the etching of both materials is possible.

The RBS/channeling spectra of a quartz surface etched with 50 pulses at  $\Phi = 0.60 \text{ J/cm}^2$  and  $\Phi = 1.00 \text{ J/cm}^2$  and a 0.5 mol/l solution of pyrene in toluene is shown in Fig. 6-4a. In addition, the spectrum of an unetched surface is included. The enhanced RBS yield of the SiO<sub>2</sub> surface labeled with Si and O are the result of a thin amorphized top layer on the surface of the etched areas. The width and the height of the peaks therefore are a measure of the degree and the depth of amorphization [98] and consequently of the modification. With the RBS simulation code RUMP [99], the thickness of the amorphous layer is estimated and depicted in Fig. 6-4b as a function of the laser fluence (simulation limitations: the degree of amorphization is assumed as 100%, no gradient in amorphization exists, minimal detector resolution: 1.2 nm amorphization depth).

The depth of amorphization increases with rising fluence (in Fig. 6-4b). The thickness of the layer is estimated to be in the range of 10 to 40 nm for  $\Phi$  = 0.60 to 1.40 J/cm<sup>2</sup>. The origin of amorphization is probably the melting of the quartz surface due to the laser irradiation. Comparing the depth of amorphization with the respectively determined values of  $\Delta h$  (included in Fig. 6-4b), the effectively removed material layer is significantly smaller than the damaged material depth.

A carbon signal that can be expected due to the deposition or incorporation of decomposition products into the amorphized layer must be visible around channel 150. The channeling spectrum for the 0.60 J/cm<sup>2</sup> etching adumbrates a carbon signal (Fig. 6-4a) but the changing in the chemical composition of the surface is not clearly visible in the spectra. If the major amount of carbon is deposited or incorporated within a layer of about 1 to 2 nm the sensitivity of the instrument [98] is probably the limit for the detection of carbon contamination. In a former experi-



Fig. 6-4: a) RBS/channeling spectra of crystalline quartz surfaces etched with  $\Phi = 0.60 \text{ J/cm}^2$  and 1.00 J/cm<sup>2</sup> (N = 500, 0.5 mol/l solution of pyrene in toluene). b) Amorphous layer thickness and  $\Delta h$  of quartz as function of the laser fluence. (The error bars in the case of amorphous layer thickness denote uncertainty of data due to detector resolution. The lines are used to guide the eyes.)

ment, a small scanned laser spot was applied and a significant contamination of the amorphized layer with carbon was found [16, 68]. The reason for a larger amount of carbon in the case of scanning is the deposition of decomposition products preferable at the edges of the irradiated area (section 5.1) that generates a thin film in front and back of the laser spot [16].

#### 6.2 Optical properties of processed fused silica sample

The visible surface modification of fused silica after LIBWE must alter the optical properties of the materials, too. A suitable parameter that indicates such optical variations presents the reflectance of the solid-liquid interface [109]. Applying a pump-probe set-up (see section 4.3.8) the reflectance measurements can be carried out in situ. Beside reflectance, also the specific absorbance of the modified layer is of great importance for discussion and modeling the LIBWE mechanism. Thus, transmittance measurements by UV/VIS spectrophotometer are applied.

#### 6.2.1 Reflectance measurements at solid-liquid interface

Fig. 6-5 presents the change in reflectance after 50 pulses in dependence on the laser fluence. The reflectance data are normalized to the reflectance of a pristine solid-liquid interface. A 0.5 mol/l solution of pyrene in toluene is applied as ab-



Fig. 6-5: Reflectance changes due to 50 laser pulses as well as the values of  $\Delta h$  and roughness (measured with WLIM at  $(11 \cdot 11) \mu m^2$ ) in dependence on the laser fluence. (The lines are used to guide the eyes.) The separation into the two fluence regions is depicted: low fluence region (1) and middle fluence region (2). (The error bars in the case of reflectance changes denote scattering of data due to the stability of the probing laser.)

sorbing liquid at  $\lambda = 248$  nm. Additionally, the respective values of  $\Delta h$  and roughness of fused silica are depicted. The etch threshold is determined to be about 0.40 J/cm<sup>2</sup>. Taking into account the roughness of the etched surface and the efficiency of etching (not presented in the figure), the middle fluence region (2) for the applied experimental conditions follows the low fluence region (1) at laser fluences larger than 0.80 J/cm<sup>2</sup>. Exceeding the etch threshold the reflectance of the interface increases as the result of an optical relevant surface modification with a certain thickness. For larger fluences, the reflectance increases ( $\Phi \approx 0.80$  J/cm<sup>2</sup>) and decreases again in region (2).

Fig. 6-6 shows the change in reflectance of the solid-liquid interface in dependence on the number of pulses for different laser fluences;  $\Phi = 0.39 \text{ J/cm}^2$  is in the range of the estimated threshold,  $\Phi = 0.66 \text{ J/cm}^2$  represents the low fluence region (1), and 1.03 J/cm<sup>2</sup> is in the middle fluence region (2). With the pump-probe set-up, a direct measure of the reflectance after each laser pulse without disturbing the experiment is possible. This allows an in situ view into the process of surface modification as a function of the pulse number. The effect of scattering on the reflected intensity of the probe laser due to the beginning evolution of surface roughness is negligible due to the only small values of rms (smaller than 2 nm) in particular for the first 100 pulses (AFM measurements, Fig. 5-4b).



Fig. 6-6: Reflectance change as a function of the applied number of laser pulses at different laser fluences. (The lines are used to guide the eyes.)

With increasing pulse number, the reflectance increases up to a maximum, decreases abruptly, and keeps almost constant for 0.66 and 1.03 J/cm<sup>2</sup>. In an additional experiment, the pulse number at which the etching begins was investigated ex situ [100]. Applying a fluence of 0.39, 0.66, and 1.03 J/cm<sup>2</sup>, the etching process of the material starts at 60, 10, and 2 pulses, respectively. At similar quantities of pulse number, the maxima in reflectance are observed (Fig. 6-6). Since the reflectance rise can be discussed as an increasing surface modification, its amount must reach first a sufficiently large value before the etching can start. Additionally, the observed increase of the surface modification during the first applied pulses (as can be seen in Fig. 6-6 for  $\Phi = 0.39$  and 0.66 J/cm<sup>2</sup>) suggests a growing thickness without a distinct interim removal of the layer.

The measured behavior of the reflectance after the starting etching process reveals related to the behavior of  $\Delta h$  in dependence on the number of applied pulses (section 5.2, Fig. 5-4b). Similar to the saturation of  $\Delta h$ , the change in reflectance keeps almost constant and gives evidence that the etching process achieves an equilibrium state after a fluence-specific pulse number. Thus, the behavior of  $\Delta h$  can be related to the modification of the surface, too.

The interpretation of the recorded reflectance data is difficult because the optical thickness of the modified layer  $(n^{I} d^{I})$  can be altered twofold by the refractive index as well as by the thickness of the modified layer. In addition, an effect of the roughness as well as a gradient in refractive index across the modified layer can be expected. An approximation for the reflectance *R* in dependence on  $(n^{I} d^{I})$  can be made with the law of refraction for reflection at a thin, non-absorbing single layer according to [101]:

$$R = \frac{r_1^2 + r_2^2 + 2r_1r_2\cos\left(\frac{2\pi}{\lambda} 2n^l d^l\right)}{1 + r_1^2 + r_2^2 + 2r_1r_2\cos\left(\frac{2\pi}{\lambda} 2n^l d^l\right)} ,$$
(6-1)

with:

$$r_1 = \frac{n^S - n^I}{n^S + n^I}$$
;  $r_2 = \frac{n^I - n^L}{n^I + n^L}$ . (6-2)

Fig. 6-5 shows a significant difference in reflectance between the low and middle fluence region. As typical values of *R* in the low fluence and middle fluence region, a 4 times and 2.5 times increase in reflectance are evaluated, respectively, regard-

ing a reflectance of 0.02% for pristine solid-liquid interface. The Raman and XPS spectra of etched fused silica (Fig. 6-2 and Fig. 6-3) reveal the deposition or incorporation of carbon products. The RBS/channeling measurements give evidence for an increasing thickness of structural damage with increasing fluence (Fig. 6-4b).

The thickness of the modified layer can be roughly approximated employing (6-1) with the refractive indices of fused silica ( $n^{S}$ ) and toluene ( $n^{L}$ ) at 810 nm (*Table A 1*, *Table A 2*) and the refractive indices of carbon ( $n^{I} \approx 1.8$  to 2.2 [126]) and defectenriched fused silica ( $n^{I} \approx 1.7$  to 1.9 [127]), respectively. The typical values of *R* in the low and middle fluence region are reached if  $d^{I}$  adds up to 30 to 70 nm and 40 to 120 nm, respectively. Thus, the approximated optical thickness from the reflectance data reveals a growth of the depth of modification with the fluence.

#### 6.2.2 UV/VIS spectroscopy

Fig. 6-7a shows UV/VIS transmission spectra (200 nm to 800 nm) of etched fused silica plates. The samples are etched with different laser fluences at  $\lambda$  = 248 nm applying 50 pulses and a 0.5 mol/l solution of pyrene in toluene (subsection 4.4.3). An ultrasonically cleaning procedure is carried out to remove only loosely bounded particles and residuals from the organic liquid. Two main results are obvious: (i) in particular in the UV spectral region, the transmittance of the etched samples is much less than that of pristine fused silica samples that have – due to the correction to the reference sample – a transmittance of 1.0 and (ii) the magnitude of the transmittance depends on the laser fluence for etching.

In the NIR spectral region (about 800 nm), the transmittance of the sample etched with 0.76 J/cm<sup>2</sup> is comparable with that of the pristine sample. The transmittance at 800 nm is slightly reduced to about 0.87 and 0.70 for fluences of 0.32 and 0.23 J/cm<sup>2</sup>, respectively. The transmittance behavior in the UV/VIS spectral region differs between the diverse laser fluences: while for the fluence of 0.76 J/cm<sup>2</sup> the transmittance steadily decreases with decreasing wavelength, a peak structure with a maximum at about 250 nm can be found for a laser fluence of 0.23 J/cm<sup>2</sup>. Such a characteristic peak in spectrum is typical for the presence of carbon products, particularly amorphous carbon [126], whereas the continuously decreasing transmittance reveals the spectrum of defect-enriched fused silica [127]. The transmission spectrum of the sample etched with 0.32 J/cm<sup>2</sup> is probably a superposition of the spectra of amorphous carbon and defect-enriched fused silica.

For calculating the absorbance from the transmittance measurements, the effects of reflection at the interfaces and scattering have to be considered according to:

$$1 = T_{op} + A + S + R , (6-3)$$



Fig. 6-7: a) UV/VIS transmission spectra (200 nm to 800 nm) of laser-etched fused silica samples at different laser fluences. The samples have been cleaned ultrasonically. The peaks at 360 nm and 530 nm are artifacts from the spectrometer. The solid lines present fits of the transmittance data of  $\Phi = 0.76$  and  $0.32 \text{ J/cm}^2$  concerning the wavelength dependence of the scattering (Rayleigh scattering). b) Approximated absorbance at 248 nm in dependence on the laser fluence before (open square symbol) and after (open triangle symbol) wiping with a soft tissue. (The error bars denote the scattering of transmittance data. The lines are used to guide the eyes). Additionally, the respective values of  $\Delta h$  and roughness (rms; measured with WLIM) are shown.

with the absorbance A, the transmittance  $T_{op}$  and the scattered part S.

The approximations from the reflectance data (Fig. 6-5) employing (6-1) give a maximal thickness of the modified layer of about 120 nm. The losses in the intensity of transmission due to the reflection at the modified layer can be approximated applying (6-1) and the respective refractive indices of amorphous carbon [126] and defect-enriched fused silica [127] to maximal 0.017 which is within the estimated experimental error of 0.03. To rule out the effect of scattering due to enhanced surface roughness on the transmission spectra, the transmittance of the samples has been measured with an integrating sphere assembly installed in the spectrometer. The same dependences of the transmittance on the wavelength have been found applying this set-up that eliminates scattering losses. Thus, the measured reduced transmittance must be caused by the absorption of the sample. This explains in addition, that the received spectra significantly differ from ones that can be expected if the transmittance is affected by a wavelength dependence of the scattering as the line fits in Fig. 6-7a show.

Fig. 6-7b presents the absorbance (A) at  $\lambda$  = 248 nm of the etched fused silica samples after ultrasonically cleaning (open square symbol) in dependence on the laser fluence that has been employed for sample preparation. In addition, the respective values of  $\Delta h$  and roughness (rms) are included in the graph. Below 0.32 J/cm<sup>2</sup>, no etching takes place for the applied number of pulses and spot size of the laser beam. Nevertheless, a large absorbance of 0.62 to 0.58 can be recognized for fluences of 0.23 and 0.27 J/cm<sup>2</sup>, respectively. For  $\Phi < 0.23$  J/cm<sup>2</sup>, no modification of the surface has been observed after 50 laser pulses. At  $\Phi = 0.32$  J/cm<sup>2</sup>, a very weak and only partially etching can be observed which is typically for LIBWE at fluences near the etch threshold (section 5.1). At fluences between 0.32 and 0.45 J/cm<sup>2</sup>, the etching process is characteristic for the low fluence region (small  $\Delta h$ , large roughness) and the respective value of absorbance decreases from 0.48 ( $\Phi = 0.32 \text{ J/cm}^2$ ) to an almost constant value of 0.37 ( $\Phi = 0.39$  and 0.45 J/cm<sup>2</sup>). For  $\Phi \ge 0.51$  J/cm<sup>2</sup>, the etching is characteristic for the middle fluence region due to the almost linear increase of  $\Delta h$  and smaller values of roughness. Here, the absorbance decreases slightly from 0.37 to 0.31 (Fig. 6-7b).

The surface of the fused silica samples is modified due to the laser-induced etching process in such a manner that the optical properties of the material alter signifi-

cantly. In coincidence with the reflectance measurements (Fig. 6-5), the absorbance corresponds to the etch behavior with its different fluence regions. The strong absorbance may cause an effective deposition of the energy of the laser pulse directly at the interface and may therefore induce large temperatures and consequently a thermal based etching of the material. Otherwise, the already large absorbance that has been generated at the laser fluences below the etching threshold is not sufficient to induce an etching effect (open square symbols in Fig. 6-7b). As described in subsection 6.1.1, the processed areas of the samples are brown or black colored due to the laser-induced surface modification even after ultrasonically cleaning procedure. If the surface of the sample is wiped with a soft tissue the coloring and therefore the visible modification of the surface can be much reduced for the places where fluences below the etch threshold have been applied. For larger fluences, e.g., in the middle fluence region, the coloring remains almost equal and can be removed only by the cleaning procedure with the oxygen plasma (see subsection 4.4.2). The resulting absorbance after wiping the samples with a soft tissue is shown in Fig. 6-7b (open triangle symbols) in dependence on the laser fluence. In comparison to the data points which are obtained before wiping, the absorbance after wiping is reduced. Now, below the threshold fluence  $(0.32 \text{ J/cm}^2)$  the absorbance is small and increases with the fluence (from 0.12 to (0.32). Afterwards, the behavior of the absorbance data with the fluence is similar to that before wiping but the values are generally smaller. The so estimated dependence of the absorbance on the laser fluence is consistent with the estimated change in reflectance in Fig. 6-5 as another optical property of the etched surface.

Fig. 6-8 shows the measured absorbance at  $\lambda = 248$  nm of a fused silica sample etched with  $\Phi = 0.76$  J/cm<sup>2</sup> after wiping with a soft tissue in dependence on the number of pulses. Additionally, the respective averaged etch depth per laser pulse is shown. For the 1<sup>st</sup> and 2<sup>nd</sup> laser pulse, no materials erosion has been observed but the absorbance increases to 0.27 and 0.30, respectively. For the first etching pulses (N = 3 and 5), the absorbance reaches a maximal value of 0.3. Subsequently, the absorbance decreases with further increasing pulse number. This behavior is similar to the measured reflectance in dependence on the pulse number (Fig. 6-6).

On the other side, it is remarkable that the absorbance decreases while the averaged etch depth per laser pulse increases with the number of applied pulses at



Fig. 6-8: Absorbance change (left axis) as a function of the applied number of laser pulses at a laser fluence of 0.76 J/cm<sup>2</sup> after wiping with a soft tissue. Additionally, the averaged etch depth per pulse  $\Delta h$  (right axis) is shown. (The lines are used to guide the eyes.)

constant laser fluence (Fig. 6-8). Furthermore, the absorbance decreases also with increasing laser fluence in the middle fluence region (Fig. 6-7b) while the RBS measurements show an increase of the thickness of structural modification with the laser fluence (Fig. 6-4b). Consequently, the kind of modification that affects the absorbance of the sample must be altered probably during the prolonged processing; at smaller fluences a chemical alteration due to the products of liquids decomposition dominates the modification while at larger fluences a structural damage of the sample causes the value of absorbance. In any case, both mechanisms should occur simultaneously and are superimposing in their effect on the absorbance measurement.

#### 6.3 Analysis of laser-irradiated liquid

A fused silica sample in contact with a 0.5 mol/l solution of pyrene in toluene is irradiated with 32000 pulses at  $\lambda = 248$  nm,  $\Phi = 0.98$  J/cm<sup>2</sup>,  $A_S = (140 \cdot 140) \mu m^2$ , and  $f_p = 100$  Hz. During the extensive laser exposure, two effects can be observed inside the liquid as a result of the laser-induced decomposition: the formation of permanent bubbles and a concomitant coloring of the liquid to deep black due to the generation of particles. The vapor bubbles, which contain also gaseous products resulting from the decomposition, could not be analyzed in situ. In the litera-

ture, hydrocarbons, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>, are found [57]. In this work, the exposed liquid without black particles is analyzed by GC-MS ion trap system whereas the black particles are examined by SEM/TEM and Raman spectroscopy.

#### 6.3.1 Chemical analysis of the liquid

Fig. 6-9 presents the received total ion current chromatogram of the exposed and unexposed 0.5 mol/l solution of pyrene in toluene. Before irradiation, the chromatogram of the liquid features with 1 and 16 only the two peaks that stand for toluene and pyrene, respectively. After laser exposure, the GC-MS analysis reveals that the very major component in the decomposition is bibenzyl (peak no. 12); the other aromatic hydrocarbons being produced are in significantly smaller yields. Xylene (2), benzaldehyde (3), benzyl alcohol (4), methyl phenol (6), benzenedimethyl (7), naphthalene (8), dimethylbiphenyl (9), diphenylmethan (10), 1-ethyl-2-phenylbenzene (11), o-benzyl toluene (13), p,p'-bitoluene (14), dibuthyl phthalate (15), and diisooctyl phthalate (17) are determined. Apart from these unambiguously identified compounds, a number of others escaped categorization whose peaks are shown in Fig. 6-9.

The main product in the decomposition of toluene (bibenzyl) reveals that the do-



Fig. 6-9: Comparison of total ion mass chromatogram of 0.5 mol/l solution of pyrene in toluene before and after laser irradiation. Peak No., compound: 1, toluene; 2, xylene; 3, benzaldehyde; 4, benzyl alcohol; 5, ambiguous compound; 6, methyl phenol; 7, benzenedimethyl; 8, naphthalene; 9, dimethylbiphenyl; 10, diphenylmethan; 11, 1-ethyl-2-phenylbenzene; 12, not attributed; 13, obenzyl toluene; 14, p,p'-bitoluene; 15, dibuthyl phthalate; 16, pyrene; 17, diisooctyl phthalate.

minant steps of the early stage of these processes are  $C(sp^2)$ -H and  $C(sp^3)$ -H fissions to produce benzyl radicals [57]. The recombination of the radicals is accompanied by a variety of other reactions considering the formation of the aromatic hydrocarbons and graphitic and polymeric carbon [57]. Decomposition products of pyrene molecules, such as cyclohexylaryl derivates [128], are not visible in Fig. 6-9. This will be related to the only small concentration of pyrene molecules compared with the presence of toluene molecules (pyrene:toluene = 1:19) and additionally to the high stability of pyrene molecules against photo degradation [129].

As a consequence of the changed composition of the absorbing liquid, the coefficient of linear absorption varies, too. The spectrophotometric measuring of the coefficient yields an increase from  $11.0 \cdot 10^3$  cm<sup>-1</sup> to  $14.0 \cdot 10^3$  cm<sup>-1</sup>, which is prob-



Fig. 6-10: Raman spectra (a), SEM (b), and TEM (b) images of particles from a laser-irradiated pyrene in toluene solution.

ably not significant for the etching regarding the conclusions made in section 5.5.

#### 6.3.2 Investigation of the solid particles

The analysis of the black particles as result of decomposition of the liquid reveals carbon as the predominant compound. The Raman spectra of the carbon products (Fig. 6-10a) show similar double-peaked structure like the spectrum of the etched fused silica sample in Fig. 6-2 with the peaks at about 1600 cm<sup>-1</sup> (*G* line) and about 1350 cm<sup>-1</sup> (*D* line). Fig. 6-10b shows a SEM image of a carbon particle. It seems that smaller particles agglomerate to the larger body. The high magnifying TEM image Fig. 6-10c gives the indication that the carbon soot consists in the mean of turbostratic carbon [130]. This is a type of crystalline structure where the crystal planes have slipped sideways relative to each other, causing the spacing between planes to be greater than ideal [130]. Electron probe microanalysis and XPS measurements show a silicon signal beside carbon that gives evidence for products from materials etching of fused silica in the soot.

#### 6.4 Summary of solid and liquid analytics

The modification process of the surface due to the effect of liquids decomposition is confirmed due to the analytics on both absorbing liquid and transparent solid. The decomposition of pyrene in toluene solution results in the formation of a multitude of aromatic hydrocarbons as well as graphitic and polymeric carbon. These carbon modifications form a film of carbon onto the previous irradiated fused silica surface. After exceeding the etch threshold, an incorporation of carbon also into the fused silica surface is indicated by the presence of the silicon carbide and the silicon-oxy-carbide bonds in XPS spectra. Hence, not alone the deposition of carbon on the surface modifies the interface but also structural changes due to the large temperature and pressure modify the surface.

The depth of modification is larger than the respective value of  $\Delta h$  but it increases in a similar manner with the laser fluence. On the other side, the strength of modification, which can be characterized by the reflectance and the absorbance of the sample surface, offers a dissimilar behavior with  $\Delta h$  and consequently with the modification depth: both properties decrease with the laser fluence by the transition from the low to the middle fluences and beyond. The Raman measurements show that this effect is caused by a changing mechanism of surface modification. At small fluences, the deposition of a carbon layer dominates the surface modification process whereas for larger fluences the fused silica itself - directly defect-enriched due to the large temperatures and pressures- is supposed as the ruling process of absorbance alterations.

### 7 The effect of surface modification on the etching

In chapter 5 and 6, a modification of the surface is suggested and confirmed by the analytical measurements. Thus, the proposed thermal etch mechanism (section 3.3) must be extended by the effect of an enhanced interface absorbance. But before the etch mechanism will be discussed, the influence of an absorbing layer on the etching process has to be verified by additional experiments.

#### 7.1 Incubation processes at LIBWE

## 7.1.1 The dependence of the threshold fluence on the pulse number and the spot size of the laser beam

The determination of material erosion thresholds is of key importance for laser processes itself. The threshold fluence is a characteristic physical value, which is constant for a given set of experimental conditions (e.g. pulse number and laser spot size) [17]. In the case of pulsed laser ablation of transparent solids, the term incubation usually describes the influence of the pulse number and the spot size of the laser beam on the threshold fluence [17, 29, 104]. The incubation effect is attributed to a modification of the material during the initial laser pulses (also called incubation pulses). In particular, laser-generated defects may enhance the absorbance of the material for the irradiating laser wavelength (subsection 2.2.2).

For direct laser ablation, a defect-dominated mechanism of incubation is discussed, which assumes that laser-generated defects are responsible for the enhanced absorption of the laser beam in the transparent material [104, 131-133]. The phenomenological model is based on the probability that the laser beam hits randomly distributed intrinsic or laser-generated defects. It is usually applied to explain reduced threshold fluences at direct laser ablation of dielectrics in air with fs [104, 131] or ns [132, 133] pulses. Beside the defect-related incubation mechanisms, the effect of thermal accumulation is discussed in the literature as another model [134]. After every laser pulse, even for those with fluences below the single shot threshold, energy is deposited in the material. If the pulse repetition rate is large enough, heat accumulation from the previous pulses occurs that increases the temperature within the irradiated spot size of the laser beam. But the application of the thermal accumulation model to LIBWE experiments seems not feasible because in the case of the LIBWE configuration an accumulative heating of the solid is possible only up to the boiling point of the liquid. According Ref. [134],  $\Phi_{th}$  depends in addition to the pulse number and the spot size on the pulse repetition rate and the sample thickness, too, which is not confirmed for LIBWE in additional experiments. By varying the repetition rate between 1 and 40 Hz the threshold fluence is constant at  $0.33 \pm 0.04$  J/cm<sup>2</sup>. Only for larger repetition rates (up to 100 Hz),  $\Phi_{th}$  decreases slightly. By use of samples with a thickness from 0.38 mm to 5 mm, no differences in the etch threshold have been found. In addition, measurements with a thermocouple inside the liquid show no temperature effect due to thermal accumulation for large pulse numbers and large repetition rates.

As Fig. 7-1a and b show, the threshold fluence for the etching of fused silica by means of LIBWE is reduced with increasing pulse number and spot size. This behavior is similar to direct ablation with laser pulses of ns [132, 133] and fs duration [104, 131, 134]. Fig. 7-1a illustrates the values of  $\Phi_{th}$  versus the numbers of laser pulses for a constant spot size ( $A_s = (100 \cdot 100) \mu m^2$ ). After 10 laser pulses,  $\Phi_{th}$  drops to about 50% of the single shot level of  $\Phi_{th}(1) = 1.10 \pm 0.17 \text{ J/cm}^2$ . A saturation of the threshold fluence is observed for pulse numbers larger than 2000 with a minimal laser fluence of  $0.22 \pm 0.025 \text{ J/cm}^2$ . For laser spot sizes  $A_s$  increasing from 400  $\mu m^2$  to 422500  $\mu m^2$ ,  $\Phi_{th}$  is reduced from 0.52  $\pm 0.05 \text{ J/cm}^2$  to 0.30  $\pm 0.033 \text{ J/cm}^2$  (Fig. 7-1b) at a constant laser pulse number (N = 300).

In the case of LIBWE, a discussion of the origin and kind of defects has to be adapted to the process because the experimentally determined threshold fluences to initiate backside etching (Fig. 7-1) are far below the ablation thresholds for direct ablation in air that are related to the occurrence or generation of point defects [29, 65]. Thus, another type of defects seems to be responsible for the incubation. As concluded from the surface-analytical and optical measurements in sections 6.1 and 6.2, deposits from liquids decomposition already cover the irradiated surface before etching occurs. That means a modification of the surface takes place at fluences below  $\Phi_{th}$  or at pulse numbers smaller than the number of incubation pulses at a given fluence. The film can be assumed as an areal defect instead of the point defects.

The reduction of  $\Phi_{th}$  with increasing pulse number in LIBWE (Fig. 7-1a) indicates a defect accumulation during the progressive laser irradiation, which can be de-

scribed by an increasing absorbance *A* due to a growing thickness of the modified layer at interface,  $d^{I}$ , with a respective absorption coefficient,  $\alpha^{I}$ :

$$A = 1 - \exp(-\alpha^{I} d^{I}) = 1 - \exp(-abs)$$
(7-1)  
(The variable  $abs = \alpha^{I} d^{I}$  is included only for mathematical operation.)

With concerning the measurement of reflectance and absorbance in dependence



Fig. 7-1: Experimentally determined threshold fluence (symbols) in dependence on a) the number of laser pulses for  $A_s = (100 \cdot 100) \,\mu\text{m}^2$  and b) the spot size of the laser beam for N = 300. A 0.5 mol/l solution of pyrene in toluene is applied as absorbing liquid at  $\lambda = 248$  nm. Additionally, the best fit by defect model in (7-11) is included in a) as solid line. (The y-error bars denote the uncertainty in determining  $\Phi_{th}$ . The x-error bars denote uncertainty due to the lack of experimental data in the quantity of investigated pulse numbers and spot sizes.)

on the number of applied laser pulses in Fig. 6-6 and Fig. 6-8, the following mechanism of incubation can be discussed. The energy of the first laser pulse is absorbed in a liquid volume that is defined by the laser spot size  $A_s$  and  $d_{\alpha}^{L}$ . The induced rise in temperature does not exceed the critical temperature for materials erosion. However, molecules fragmentation inside the irradiated volume of the liquid takes place [57, 59] and leads to the observed deposits (Fig. 5-2a and Fig. 5-3). The subsequent laser pulse is now absorbed by the layer and, thereafter attenuated in the layer, by the liquid. If the laser-induced temperature exceeds the critical temperature, etching takes place. If the induced temperature is too small, both the solid surface and the deposited layer remain intact. In this case, additional decomposition products are deposited and increase the thickness of the layer and consequently its absorbance for the next laser pulse. With rising number of incubation pulses, the absorbance of the interface region increases without interim removal of the layer up to a sufficient value to induce the critical temperature at the interface for fused silica etching.

According to Ref. [38], the laser-induced temperature raise of the solid surface is proportional to the absorbed fluence that depends on the absorbance of the layer:

$$\Delta T_c = k I A = k \Phi A \tau_p^{-1} \quad . \tag{7-2}$$

Concerning (2-8), the proportionality factor k must summarize the thermal properties ( $\rho$ ,  $c_p$ , and  $\kappa$ ) of both the solid and the liquid and has the unit (K cm<sup>2</sup> s)/J. The critical temperature rise  $\Delta T_c$  required for the etching is constant for one specific material. Thus, with combining (7-1) and (7-2) the relation between  $\Phi_{th}$  and A is:

$$\Phi_{th}(N) = \frac{\tau_p \,\Delta T_C}{k \,A(N)} = \frac{\tau_p \,\Delta T_C}{k \,\{1 - \exp[-abs(N)]\}} \ . \tag{7-3}$$

According to (7-3), the threshold fluence must depend on the absorbance of the materials surface as a function of the number of pulses. (The materials properties k and  $T_c$  and the duration of the laser pulse are here defined as constant.)

With rising number of pulses, *A* initially increases and converges asymptotically to a critical value necessary to induce the critical temperature for the etching. The discrete increase of absorbance per laser pulse must decrease with the number of pulses because the layer deposited due to the previous laser pulse attenuates the laser radiation. The lower transmitted fluence reduces the amount of lasergenerated decomposition products inside the liquid volume that contribute to the growth of the layer. For mathematical operations, the variable *abs* (7-1) instead of the laser-generated absorbance of the sample is used. When the deposition of the absorbing layer is originated from a photochemical process, the diminished absorbance with the time under the consideration of the attenuation of the laser beam in the layer is given by:

$$\frac{d\ abs}{dt} = \mu^{\Phi th} I_0 \exp(-abs) \quad , \tag{7-4}$$

with  $\mu^{\Phi_{th}}$  as the rate constant for the film deposition. For calculating the alteration of the absorbance during the incubation time  $t_{inc}$ , (7-4) has to be integrated to:

$$\int \exp(abs) \, d \, abs = \int_{0}^{t_{inc}} \mu^{\Phi th} \, I_0 \, dt \quad .$$
(7-5)

Since photochemical processes are related to the incident photon density (subsection 2.4.2), the absorbance changes only during the duration of the laser pulse. Thus, the incubation time is defined with  $t_{inc} = N \tau_p$  and (7-5) can be written as:

$$\exp(abs) + c_1 = \int_{0}^{N \tau_p} \mu^{\Phi th} I_0 dt = N \tau_p \mu^{\Phi th} I_0 , \qquad (7-6)$$

and yields to:

$$\exp(-abs) = \frac{1}{\mu^{\Phi th} \Phi N - c_1}$$
 (7-7)

With the initial condition abs = 0 at N = 0, the integration constant  $c_1$  is given to be  $c_1 = -1$ . With (7-1) the absorbance is:

$$A(N,\Phi) = 1 - \frac{1}{\mu^{\Phi th} \Phi N + 1}$$
 (7-8)

To describe the model for the incubation-affected threshold fluence at LIBWE, (7-2) and (7-8) have to be combined and give:

$$\Phi_{th} = \frac{\tau_p \,\Delta T_C}{k} \left( 1 - \frac{1}{\mu^{\Phi th} \,\Phi_{th} \,N + 1} \right)^{-1} \,. \tag{7-9}$$

(7-9) can be transformed into quadratic equation and solved for  $\Phi_{th}$ :

$$\Phi_{th}(N) = \frac{\tau_p \,\Delta T_C}{2 \,k} \pm \sqrt{\left(\frac{\tau_p \,\Delta T_C}{2 \,k}\right)^2 + \frac{\tau_p \,\Delta T_C}{k \,\mu^{\Phi th} \,N}} \quad .$$
(7-10)

For  $N \rightarrow \infty$  and with concerning that only the summation of (7-10) results in physical relevant values,  $\Phi_{th}(N)$  in (7-10) delivers the minimal laser fluence beneath no

etching is possible (see also Fig. 7-1a;  $\Phi_{th}(N > 2000)$ ): the multi-pulse threshold fluence  $\Phi_{th}(\infty)$ . Thus, the term  $\frac{\tau_p \Delta T_C}{k}$  is given to be  $\Phi_{th}(\infty)$ . Consequently, (7-10) can be now written as:

$$\Phi_{th}(N) = \frac{\Phi_{th}(\infty)}{2} + \sqrt{\left(\frac{\Phi_{th}(\infty)}{2}\right)^2 + \frac{\Phi_{th}(\infty)}{\mu^{\Phi_{th}} N}} \quad .$$
(7-11)

Applying (7-11) to the experiment (Fig. 7-1a), the fit reflects the experimental data well with the best fit parameters  $\mu^{\Phi_{th}} = 0.2 \pm 0.02 \text{ J}^{-1}$  and with the experimentally determined multi-pulse threshold fluence  $\Phi_{th}(\infty) = 0.22 \text{ J/cm}^2$  as fixed parameter. For N = 1, (7-11) delivers the single-shot threshold  $\Phi_{th}(1) = 1.11 \text{ J/cm}^2$  that correlates with the found experimental single-shot threshold (Fig. 7-1a).

The threshold fluence depends also on the spot size of the laser as the experimental results in Fig. 7-1b show. On the other side, the proposed model summarized in (7-11) expects an independence of  $\Phi_{th}$  from  $A_s$ . From this mismatch it can be concluded that in addition to a photochemical process a photothermal process probably contributes to the modification of the surface. Such a combination of photochemical and photothermal processes is well known from the laser ablation of polymers [17]. In the case of LIBWE, the laser-induced temperatures far exceed the boiling temperature of the liquid (that causes the effect of bubble formation) and can reach temperatures larger than 1000°C [8, 12]. Due to such large temperatures, photothermal decomposition of the organic liquid seems probably.

The determined multi-pulse threshold fluence of 0.22 J/cm<sup>2</sup> (Fig. 7-1) corresponds in a good manner with the observations in subsection 6.2.2 that for  $\Phi < 0.22$  J/cm<sup>2</sup> no modification of the surface takes place. Furthermore, photoacoustic measurements by Tsuboi et al. [58] gave a threshold of toluene ablation in the range of 0.20 J/cm<sup>2</sup>. It is suggested in [58] that the threshold for toluene ablation coincides with the beginning of explosive evaporation [58]. Thus, the reduction of the threshold fluence is probably limited by the occurrence of vapor bubbles at the interface. In Ref. [108] is suggested that the laser-generated vapor bubble (subsection 2.4.1) affects the etching because the bubble contains the gaseous decomposition products [57]. The lifetime of a bubble depends on its size and consequently on the energy of the laser pulse [53, 54], which is defined by  $\Phi \cdot A_S$ . The interaction of the vapor with the surface can result in the deposition of carbon products. Thus, with increasing energy the duration of the contact between the gaseous decomposition products and the solid increases and the absorbance of the modified layer must grow [108].

#### **7.1.2** The effect of incubation on $\Delta h$

The described mechanism of incubation in subsection 7.1.1 can explain the reduction of  $\Phi_{th}$  if the deposited carbon layer remains intact and its thickness increases due to the prolonged laser irradiation. With reaching the critical absorbance to exceed  $T_c$  for materials erosion, the surface of the sample is etched. Thereby, the deposited layer is removed, too. The measured reflectance and absorbance in dependence on the pulse numbers in Fig. 6-6 and Fig. 6-8 show an abrupt decrease in both attributes (and consequently in modification) for the laser pulse that follows the pulse, which first etches the sample. Thus, the layer of decomposition products is not completely renewed but the surface is still distinctly modified. In this context, the measured transmission spectra in Fig. 6-7a reveal a change in the kind of modification from non-etching to etching: with the beginning materials erosion, the spectra are characteristic for defect-enriched fused silica whereas below the threshold spectra that are typically for amorphous carbon have been recorded. Consequently, the process of surface modification is not finalized with the beginning materials erosion. The observed nonlinear increase and finally the saturation of  $\Delta h$  with increasing number of applied laser pulses and spot size of the laser beam (Fig. 5-4a and Fig. 5-5) are probably originated from a second incubation process, which causes the structural damaging of the near surface region of the fused silica sample. Otherwise, the estimated absorbance of the sample (Fig. 6-8) decreases with the pulse number. Because the optical measurements made in section 6.2 are not able to distinguish between the two kinds of modification, an unambiguous relation between the absorbance measurements, the second incubation process (structural damaging of the sample), and the nonlinear increase of  $\Delta h$  is not possible yet.

#### 7.2 Backside etching due to carbon layer ablation

To study the contribution of a thin, highly absorbing carbon layer at the back surface of transparent sample to the etching a fused silica plate is coated on one side with a carbon layer that can absorb the laser beam (thickness:  $20 \pm 5$  nm). The

layer was prepared by scanning the laser across the fused silica back surface in LESAL set-up (section 3.2) and is well adherent (i.e., it cannot be removed ultrasonically or by wiping). Transmittance measurements by UV/VIS spectroscopy show an absorbance of the layer for  $\lambda = 248$  nm of about 0.40. The fused silica sample with the layer on the back surface is irradiated with a single laser pulse in LIBWE set-up but with an inert and non-absorbing diluted gas (air) and liquid (distilled water) as medium at the back surface.

Without the absorbing layer, no etching occurs up to fluences of about  $10 \text{ J/cm}^2$  after a single laser pulse. This correlates with the findings for direct front side ablation of fused silica in air [65] and with water film [135]. With the carbon layer, the etching threshold fluence for a single laser shot is determined to be about 0.50 J/cm<sup>2</sup> and is independent from the kind of medium. Between 0.30 and 0.50 J/cm<sup>2</sup>, only ablation of the carbon layer occurs without any visible effect on the fused silica. Below 0.30 J/cm<sup>2</sup>, the carbon film withstands laser irradiation.

In Fig. 7-2, the measured etch depth of fused silica is shown in dependence on the laser fluence after the irradiation with one laser pulse. In the case of the liquid at the back surface, the etch depth grows almost linearly with increasing laser fluence up to about 60 nm at  $\Phi = 2.20 \text{ J/cm}^2$ . Within this fluence range, a constant efficiency of about  $30 \cdot 10^{-7} \text{ cm}^3/\text{J}$  can be calculated. Exceeding  $\Phi = 2.20 \text{ J/cm}^2$ , the effi-



Fig. 7-2: Etch depth in dependence on the laser fluence after one-pulse treatment of a fused silica sample covered with a 20 nm carbon layer at the back surface. The backside is immersed in distilled water (triangle symbols) or in contact with air (circle symbols).

ciency of etching increases that results in a deep etching of 120 and 230 nm at 3.10 and 4.80 J/cm<sup>2</sup>, respectively. This behavior is similar to the observed separation into the middle and high fluence range in section 5.1. For the back surface ablation of carbon layers with air as medium at the back surface, the measured etch depth first tends to saturate to about 20 nm for fluences between 0.60 and 2.20 J/cm<sup>2</sup> and shows a fast increase for larger fluences (Fig. 7-2). An etch depth of 60 and 150 nm at 3.10 and 4.80 J/cm<sup>2</sup> is reached, respectively.

For thermal driven ablation processes of bulk materials, larger fluences cause faster heating rates and consequently larger temperatures and ablation depths per pulse [17]. Otherwise, larger temperatures due to larger fluences lead to faster desorption rates of adsorbed layers [59, 136]. In the current case, the ablation of the carbon layer at the fused silica back surface in diluted gas medium (air) results in an almost constant etch depth within a wide fluence range (Fig. 7-2). The fast laser heating of the layer probably results in a considerable heat flux from the layer to the fused silica before the layer is removed due to vaporization. Since a certain temperature is required to ablate the layer, e.g., the vaporization temperature of carbon, the further increase of the laser fluence absorbed within the layer reduces the time to remove the film without a significant change in the temperature of the fused silica surface. Thus, the time interval to heat the fused silica surface is limited by the time necessary to increase the temperature of the carbon layer above the evaporation point. The found constant etch depth in air (Fig. 7-2) gives the evidence that the flux of heat from the layer to the fused silica sample is independent from the fluence, which is probably the result of an equilibrium state between layer ablation and fused silica heating.

In contrast to back surface ablation in air, the confinement of the evaporated layer due to the liquid hinders its expansion away from the surface. Thus, the time interval to heat the fused silica sample is elongated. The confined ablation plume probably forms a region with large pressure, density, and temperature near the solidliquid interface. In particular, the temperature of the near interface region must depend on the fluence since a larger part of the energy of the laser pulse, which has been absorbed by the carbon layer, can heat the sample. Thus, the etch depth of fused silica increases almost linearly with the fluence (Fig. 7-2). The effect of confinement of the ablation plume by a liquid that results in an increased efficiency of ablation has already been reported for pulsed laser irradiation of water-covered aluminum, silicon, and carbon targets (subsection 2.4.3).

The existence of a highly absorbing layer on the back surface of a transparent sample leads to an etching of the sample due to laser irradiation [137]. Thereby, the confinement situation (diluted or dense environment) affects the backside etching effect; a denser medium may enhance the etch depth per laser pulse compared with a diluted medium and defines the characteristic behavior of the etch depth. Comparing the characteristic of the etch depth as a function of  $\Phi$  in case of back surface layer ablation with liquid confinement (Fig. 7-2) with that of  $\Delta h$  of LIBWE (Fig. 5-1) similar characteristics are visible, e.g., the separation into different fluence regions or an almost linear increase of  $\Delta h$  with the laser fluence. Additionally, the constant etch depth within a wide fluence range in case of air "confinement" coincides well with the region of etch rate saturation at LESAL processing (see section 3.2; [10]).

#### 7.3 Metallic liquid absorber

The distinct influence of the modification of the surface on LIBWE is affirmed (sections 7.1 and 7.2) but makes the modeling for temperature approximations quite difficult. The interface offers a sandwich structure that consists of solid, high absorbing layer, and absorbing liquid. To discuss a thermal-based etch mechanism, the interface has to be simplified with a liquid that offers: (i) very large (almost infinite) absorption coefficient and (ii) no laser-induced decomposition. Liquid metals, such as gallium, meet the requirements appropriately.

The etch depth per pulse and the efficiency of etching of fused silica with liquid gallium after 10 laser pulses are shown in Fig. 7-3 as a function of the laser fluence. The given values of the fluence per laser pulse are already corrected considering the high reflectance of the silica-gallium interface that was estimated with about 80%. Thus, the experimental threshold fluence of about 0.26 J/cm<sup>2</sup> is comparable to LIBWE with hydrocarbons (section 5.5).

In principle, the behavior of  $\Delta h$  and the respective *E* is similar to the results of LIBWE with organic solutions (section 5.1) concerning the separation into the low and middle fluence region. After exceeding the threshold fluence, a partial etching of the surface can be observed with very small etch rates. This results in a distinct

surface roughening [138] similar to the low fluence region found for organic liquid absorbers (section 5.5). Furthermore, the efficiency of etching increases with the fluence, too. The transition from low to middle fluence region can be determined for a fluence of about 0.54 J/cm. For larger fluences,  $\Delta h$  increases almost linearly up to an etched depth per pulse of about 620 nm/pulse at 1.60 J/cm<sup>2</sup>. Such large values of  $\Delta h$  have not been observed in LIBWE with organic liquids yet (see subsection 5.5.2) and even exceed the typical ablation rates of high absorbing solids [17]. The efficiency of etching is almost constant and is estimated to be about  $380 \cdot 10^{-7}$  cm<sup>3</sup>/J which is 30 times larger than for etching with organic solutions. However, the surface quality in the middle fluence region is rather good; the etched pits have well-defined edges and a smooth bottom [138] similar to LIBWE with the pyrene in toluene solutions. A high fluence region known from organic absorbers is not found during the experiments with liquid gallium.

By means of gallium outside the etched pit a surrounding region of some micron width with a higher roughness is observed where a small amount of gallium can be found as electron probe micro analysis reveals [138]. At the bottom of the etched pits and the virgin surface area that were also in contact with the liquid gallium no Ga-contaminations are measurable [138].





Fig. 7-3: Averaged etch depth per laser pulse  $\Delta h$  (left axis) and the efficiency of etching per laser pulse *E* (right axis) as a function of the laser fluence (considering the reflectance of the gallium). 10 pulses are applied with gallium as absorbing liquid at  $\lambda = 248$  nm.



Fig. 7-4: Schematic sketch of heat fluxes at fused silica-gallium interface.

terface offers two advantages: (i) the boiling point of gallium ( $T_B = 2200^{\circ}$ C) is larger than the proposed critical temperature for fused silica's etching that permits melting of the solid without liquid evaporation; and (ii) material alterations - rather expected due to the proposed thermal driven etch processes - do not significantly influence the absorption of the laser radiation at the solid-liquid interface because of the very large absorption coefficient of gallium ( $\alpha^L > 10^6$  cm<sup>-1</sup> [139]).

For estimating the temperature at the fused silica surface in contact with liquid gallium, the laser absorption at the interface and the heating of both gallium and fused silica has to be considered. For selecting an appropriate model for laser heating, the characteristic length has to be considered that is given either by the absorption length of the laser radiation into the material or the thermal diffusion length [17]. Due to the laser absorption in the liquid gallium, the decision on the heating confinement is derived from the material properties of gallium. In gallium,  $d_{\alpha} = (\alpha^{L})^{-1} = 10$  nm is the optical penetration depth for the laser radiation. The thermal diffusivity of gallium is 0.154 cm<sup>2</sup>/s (calculated with  $\kappa_{Ga} = 40$  W/(m K),  $c_{p} = 0.37$  J/(g K), and  $\varrho = 5.91$  g/cm<sup>3</sup> [140, 141]). Thus, the thermal diffusion length of liquid gallium for the duration of the laser pulse is about 1.2 µm that exceeds  $d_{\alpha}$  by several orders of magnitude. Consequently, the depth of dissipation of the laser energy is thermal confined, i.e., by  $d_{T}$ .

In the case of indirect laser heating of a material due to an absorber, the laser absorption in the absorber as well as the thermal flux across the interface into the transparent material (Fig. 7-4) must be considered. Thus, following boundary conditions are present:

$$T^{L} = T^{S} = T_{0}$$
  $t = 0$   
 $T^{L} = T^{S}$   $z = 0, t > 0$ 
(7-12)

with  $T^{L}$  and  $T^{S}$  as temperatures of gallium and fused silica, respectively.

To describe the temperature field in the fused silica, the relation in (2-9) for  $d_T \gg d_{\alpha}$  can be employed. The thermal fluxes into the gallium  $J^L$  and into the fused silica  $J^S$  are unknown (Fig. 7-4). The sum of the heat fluxes into the solid and the liquid is equal to the laser intensity according to:

$$J^L + J^S = I_0 (7-13)$$

The respective heat fluxes can be calculated by variation of the coefficients considering the boundary condition at the interface (7-12). The solution of the problem during the heating cycle of the laser pulse ( $0 < t < \tau_p$ ), that agrees with a solution given in [38], is:

$$\Delta T^{S}(z,t) = \frac{2 I_0 \sqrt{D^L D^S t}}{\kappa^L \sqrt{D^S} + \kappa^S \sqrt{D^L}} \operatorname{ierfc}\left(\frac{z}{2\sqrt{D^S t}}\right) .$$
(7-14)

Hence, the maximal temperature at interface (ierfc(z = 0) =  $\frac{1}{\sqrt{\pi}}$  [17]) is:

$$\Delta T^{S}(z=0,t) = \Phi(1-R) \frac{2}{\sqrt{\pi t}} \frac{\sqrt{D^{L} D^{S}}}{\kappa^{L} \sqrt{D^{S}} + \kappa^{S} \sqrt{D^{L}}} , \qquad (7-15)$$



Fig. 7-5: Calculated maximal temperatures  $T_{max}$  of the fused silica-gallium interface at  $t = \tau_p$  as a function of the laser fluence. The respective  $\Delta h$  (symbols) are included, too.  $T_c^{(1)}$  and  $T_c^{(2)}$  are the critical temperatures for etching.  $\Phi_{th}^{(1)}$  and  $\Phi_{th}^{(2)}$  are the thresholds for the beginning etching and the middle fluence region, respectively.

where the laser intensity  $I_0$  is substituted by the laser fluence (2-6) absorbed at the interface of fused silica and gallium.

The graph in Fig. 7-5 presents the calculated maximal temperature (7-15) of the heated fused silica surface. The fluence that is related to the critical temperature  $T_c^{(1)}$  (Fig. 7-5) agrees in a good manner with the estimated threshold fluence. This supports the melting point of cristobalite ( $T_M = 1720^{\circ}$ C) as the critical temperature for etching. The beginning of the middle fluence region at 0.54 J/cm<sup>2</sup> may coincide with another assumed critical temperature for the etch process  $T_c^{(2)}$ : the point of beginning vaporizing of SiO<sub>2</sub> melt ( $T_B = 2900^{\circ}$ C) [43]. Furthermore, the linear growth of  $\Delta h$  with the fluence in the middle fluence region is well fitted by the calculated maximal temperatures at interface.

In conclusion, the exploitation of a metal as liquid absorber presents a suitable model to investigate the primary processes and the thermal etch mechanism of LIBWE. Gallium offers a sufficiently high absorbance and does not decompose under intense laser irradiation. Thus, the effects from liquid decomposition on the etching can be disregarded. An analytical model is applied to calculate the temperatures at the solid-liquid interface. The computations show, that the calculated fluence necessary to exceed the critical temperature for etching agrees well with the experimentally determined one. This agreement together with the linear increase of  $\Delta h$  and the surface temperature confirm in principle a thermal etch mechanism of LIBWE.

#### 8 Discussion of LIBWE mechanism

#### 8.1 General view onto contributing processes at LIBWE

UV laser irradiation of highly absorbing organic liquids causes complex processes, such as fast and strong liquid heating, large transient pressure, boiling, bubble formation and collapse, and decomposition of the molecules of the liquid that results in materials erosion and, in addition, in surface modification (Fig. 8-1a).

The modification of the surface is based on the laser-induced decomposition of the liquid followed by deposition and incorporation of decomposition products. Additionally, the near surface region of the solid is structurally damaged probably as result of the large laser-induced temperature and pressure. Due to the alteration, the absorbance of the interface for the incident laser pulse is distinctly enhanced. Thus, the model of the solid-liquid interface has to be improved to a sandwich structure which consists of transparent solid, highly absorbing interface layer, and absorbing liquid (see Fig. 8-1b). Consequently, the laser-induced heating of the transparent solid occurs by superposition of temperature fields due to interface and liquid volume absorption.

With considering the experimental results in the chapters 5, 6, and 7, the etch mechanism of LIBWE can be formulated as followed. The first laser pulse irradiates the pristine solid-liquid interface, is absorbed by the liquid, and heats a liquid volume within the optical penetration depth  $d_{\alpha}^{L}$ . Due to the small thermal diffusion



Fig. 8-1: a) Sketched processes at laser-irradiated solid-liquid interface and b) optical sandwich structure of solid-liquid interface after and during irradiation which consists of transparent solid, high absorbing interface layer, and absorbing liquid.

length of organic liquids within the time duration of the laser pulse (toluene:  $d_T^L \approx 0.1 \,\mu\text{m}$ ) compared with the respective optical penetration depth  $d_{\alpha}^L \approx 1 \,\mu\text{m}$  (0.5 mol/l solution of pyrene in toluene), only the laser energy absorbed within  $d_T^L$  is able to contribute to the heating of the solid. Recent calculations of Zimmer [142] show that for  $d_{\alpha}^L \approx 1 \,\mu\text{m}$  only 2.5% of the overall energy of the laser pulse are utilized for solids heating. The remaining energy heats the liquid and causes the described effects of liquid decomposition and bubble formation. Thus, an etching with the first pulse takes place only at large fluences due to the poor energy utilization. Applying the calorimetric approach as illustrated in (3-2), a laser fluence of at least 1.20 J/cm<sup>2</sup> is necessary to exceed the critical temperature for etching at the surface. This is in a good agreement with the single-pulse etching results in subsection 7.1.1. Due to the presence of a highly absorbing interface layer, a part of the laser energy is directly absorbed at the solid surface and the heating becomes more effective than without the surface modification. Thus, the critical temperature for etching can be exceeded already at smaller laser fluences.

#### 8.2 Analytical temperature calculations at solid-liquid interface

The principle of superposition of heat fluxes can be used to find an analytical solution for the temperature at solid-liquid interface within the time duration of the laser pulse. The solution must consider the enhanced absorbance at the interface by the surface modification and the absorbance of the liquid to estimate the temperature at the interface as result of the heat fluxes into solid and liquid. This first model does not consider phase changes and temperature- or pressure-dependent material properties.

For the calculations of the temperature at the interface, the temperatures due to the two heat sources resulting from interface and liquid volume absorption have to be superimposed. Hence, the temperature raises induced by laser absorption at interface ( $\Delta T_I$ ) and in liquid volume ( $\Delta T_{LV}$ ) determine the maximal interface temperature raise as follows:

$$\Delta T_{max} = \Delta T_I + \Delta T_{LV} \quad . \tag{8-1}$$

The heating from the modified layer at interface meets the requirement for surface absorption  $(d_T^S \gg d^I)$  in a good approximation. Thus, the special solution of heat equation (7-15) can be used considering the fluence absorbed by the layer:

$$\Delta T_{I}(z=0,t) = \Phi[1 - \exp(-\alpha^{I} d^{I})] \frac{2}{\sqrt{\pi t}} \frac{\sqrt{D^{L} D^{S}}}{\kappa^{L} \sqrt{D^{S}} + \kappa^{S} \sqrt{D^{L}}} .$$
(8-2)

The description of the temperature raise at the interface induced by the heated liquid volume is much more complex [142] due to the finite absorbance of the liquid and the optical confined energy dissipation  $(d_T^L \ll d_\alpha^L)$ . An approximation of the temperature can be made regarding the heat balance of absorbed laser energy within a material volume limited by the heat diffusion lengths  $d_T^L$  and  $d_T^S$  (section 3.3). The average temperature raise due to energy absorption can be approximated according to (3-2) with:

$$\Delta T_{LV}(z=0,t) = \Phi \exp(-\alpha^{l} d^{l}) \frac{[1 - \exp(-\alpha^{L} d_{T}^{L})]}{\varrho^{s} c_{p}^{s} d_{T}^{s} + \varrho^{L} c_{p}^{L} d_{T}^{L}} .$$
(8-3)

The estimated temperatures derived for the energy balance are smaller than the real ones at the interface due to an averaging over the whole near interface region.

With (8-1), (8-2), and (8-3) the final expression for the interface temperature considering the absorbance *A* due to the modified interface is:

$$\Delta T_{max}(z = 0, t) = \Phi[C_2 + (C_1 - C_2) A] , \qquad (8-4)$$
with

$$A = 1 - \exp(-\alpha^{I} d^{I})$$

$$C_{1} = \frac{2}{\sqrt{\pi t}} \frac{\sqrt{D^{L} D^{S}}}{\kappa^{L} \sqrt{D^{S}} + \kappa^{S} \sqrt{D^{L}}}$$

$$C_{2} = \frac{[1 - \exp(-\alpha^{L} d_{T}^{L})]}{\varrho^{S} c_{p}^{S} d_{T}^{S} + \varrho^{L} c_{p}^{L} d_{T}^{L}}$$
(8-5)

In Fig. 8-2 the maximum temperatures calculated with (8-4) at the solid-liquid interface without (line labeled with A = 0.00) and with an assumed partial interface absorbance (lines labeled with A = 0.05, 0.10, 0.15, and 0.30) in dependence on the laser fluence are shown. The temperatures are estimated for the interface between fused silica and a 0.5 mol/l solution of pyrene in toluene considering the respective materials properties (*Table A 1* and *Table A 2*). Without a partial interface absorbance, the temperature exceeds a critical temperature for etching ( $T_c^{(1)} = 1720$ °C) not until a fluence of 1.15 J/cm<sup>2</sup>. This fluence value corresponds with the found single shot threshold  $\Phi_{th}^{(2)}$  (see also Fig. 7-1a) where the laser irradiates a pristine solid-liquid interface. Thus, the melting temperature of cristobalite (*Table A 1*) seems most probably as critical temperature for the beginning etching process



Fig. 8-2: Calculated  $T_{max}$  (lines) of solid-liquid interface (fused silica, 0.5 mol/l solution of pyrene in toluene) at  $t = \tau_p$  in dependence on the laser fluence. Different values for A are applied. The experimentally determined threshold fluences after 300 pulses ( $\Phi_{th}^{(1)}$ ) and 1 pulse ( $\Phi_{th}^{(2)}$ ) (sections 5.1 and 7.1.1) as well as the melting point ( $T_c^{(1)}$ ) of cristobalite (*Table A 1*) as critical temperatures for etching are included.

(section 7.3). With supposing a partial interface absorbance of 0.05, twice the temperature raise at interface and consequently solid surface can be achieved compared to that of A = 0.00. To exceed  $T_{C}^{(1)}$  at the experimentally determined threshold fluence after 300 pulses ( $\Phi_{th}^{(1)} = 0.33$  J/cm<sup>2</sup>, Fig. 5-1a), a minimal absorbance at the interface of 0.10 is necessary.

In Fig. 8-3, the contribution of the interface heat source ( $\Delta T_I$ ) and the liquid volume heat source ( $\Delta T_{LV}$ ) onto the interface temperature  $\Delta T_{max}$  are pointed out with respect to the increasing absorbance at the interface. The laser fluence is fixed and the temperatures are normalized onto the maximal possible temperature (A = 1.0). Since  $\Delta T_{max}$  and  $\Delta T_I$  increase with rising absorbance,  $\Delta T_{LV}$  must decrease simultaneously. The right axis in Fig. 8-3 shows the ratio of  $\Delta T_{LV}$  and  $\Delta T_{max}$  and emphases the importance of the surface modification on the LIBWE mechanism; at A = 0.06and 0.20 the contribution of  $T_{LV}$  to  $T_{max}$  decays to 1/e and 1/e<sup>2</sup>, respectively. At A = 0.35 as typical value of absorbance due to the surface modification (subsection 6.2.2), the ratio  $T_{LV}/T_{max}$  becomes 0.07. In consequence, an only small absorbance at the interface is more effective than a large absorption coefficient of the liquid. Nevertheless, the liquid initiated the surface modification due to the laser irradiation. Thus, for an appropriate choice of the liquid, the ability to form an ab-



Fig. 8-3: Calculated temperatures  $\Delta T_{l}$ ,  $\Delta T_{LV}$ , and  $\Delta T_{max}$  for  $t = \tau_p$  according to (8-2), (8-3), and (8-4) in dependence on the interface absorbance A. The laser fluence is fixed and  $\Delta T_l$ ,  $\Delta T_{LV}$ , and  $\Delta T_{max}$  are normalized to  $\Delta T_{max}$  at A = 1.00. The right axis shows the percentage of  $\Delta T_{LV}$  contributing to  $\Delta T_{max}$ .

sorbing layer at the solid-liquid interface is important.

The incubation effect at LIBWE for progressive pulsed irradiation is caused by the increasing absorbance at the solid-liquid interface up to a sufficient value to exceed the critical temperature for etching (subsection 7.1.1). To calculate the threshold fluence as a function of arbitrary partial interface absorbance, the relation in (8-4) can be used in a transposed form:

$$\Phi_{th} = \left[\frac{\Delta T_C}{(C_1 - C_2)A + C_2}\right]$$
(8-6)

The necessary laser fluences to exceed  $T_c$  are calculated with (8-6) and depicted in Fig. 8-4 for fused silica and a 0.5 mol/l solution of pyrene in toluene as solid-liquid interface. As expected, the threshold fluences decrease with increasing *A*. At pristine fused silica surface (A = 0.0), the etch threshold is calculated to be about  $1.15 \text{ J/cm}^2$ . This value corresponds well with the found single shot threshold fluence  $\Phi_{th}^{(2)}$  in Fig. 7-1. At the experimentally determined multi-pulse threshold fluence  $\Phi_{th}^{(1)} = 0.22 \text{ J/cm}^2$ , an absorbance of about 0.17 is necessary to reach  $T_c$ . A reduction of the threshold fluence beneath the found multi-pulse threshold is possible when *A* will be further enhanced. On the other side, if the laser fluence is less than a liquid-specific value, no liquid decomposition and consequently no surface modification take place (subsection 6.2.2). Thus, the liquid probably defines the



Fig. 8-4: Calculated threshold fluence for  $t = \tau_p$  to exceed the critical temperatures for materials etching using (8-6) in dependence on the partial interface absorbance *A* (fused silica, 0.5 mol/l solution of pyrene in toluene). The dashed lines point out the experimentally determined multipulse threshold  $\Phi_{th}^{(1)}$  and the single-pulse threshold  $\Phi_{th}^{(2)}$ .

minimal threshold fluences at LIBWE.

In Fig. 8-5, the induced temperature raise  $\Delta T_{max}$  at the interface between fused silica and a 0.5 mol/l solution of pyrene in toluene is calculated with (8-4). For the calculations, the experimentally estimated absorbance of the sample after wiping with a soft tissue (Fig. 6-7b) is considered as A of the interface layer. Additionally, the respective etch depth per laser pulse is shown. The calculated temperatures at the interface are distinctly larger than the proposed critical temperature for etching of 1720°C; for  $\Phi > \Phi_{th}$ ,  $T_{max}(z = 0, t = \tau_p)$  increases from 4200 to 8500°C for the measured respective absorbance but follows the increase of  $\Delta h$  with the fluence. Since the absorbance is measured after applying 50 laser pulses (subsection 6.2.2), the etch process has began earlier and the modification of the surface is probably advanced due to the second incubation process (subsection 7.1.2). Consequently, the calculated temperature at  $\Phi = 0.32 \text{ J/cm}^2$  (the smallest laser fluence at which after 50 pulses a measurable etching occurs) can be larger than the proposed value of the critical temperature. In the case of  $\Phi < \Phi_{th}$ , the temperatures are already larger than  $T_{c}$ , too. On the other side, the very large temperatures below and at the threshold fluence become plausible, if the point of beginning vaporizing of  $SiO_2$  $(T_B = 2900^{\circ}\text{C})$  [43] is considered as the critical temperature for etching instead of



Fig. 8-5: Calculated temperatures in dependence on laser fluence for  $t = \tau_p$  by means of (8-6) of solid-liquid interface (fused silica, 0.5 mol/l solution of pyrene in toluene) considering the experimentally determined absorbance data (subsection 6.2.2). The respective etch depths per pulse are included. (The lines are used to guide the eyes.)

the melting point. In this case, the calculated temperature at  $\Phi_{th}$  is larger than  $T_c$  while the calculated temperatures for  $\Phi < \Phi_{th}$  are smaller. On that condition, in Fig. 8-5 an appropriate relation between the analytical temperature model, the experimentally measured etch threshold, and the estimated surface absorbance of the modified samples is presented.

# 8.3 The discussion of the etch process by an improved model of LIBWE

As shown in the chapters 5, 6, and 7, the mechanism of LIBWE is very complex. Transient photochemical and photothermal processes are involved and may interact to each other. The optical, chemical, and structural properties of both the solid and the liquid are altered due to a prolonged laser irradiation (incubation). Therefore, only the most important situations of the LIBWE process will be discussed to establish an improved model of the etching process.

For a pristine solid-liquid interface, the etch mechanism as proposed by the literature [8, 72, 73] is a sequence of heating the solid surface by the laser-heated liquid up to  $T_c$  followed probably by a mechanical removing of the molten or softened layer. But, this mechanism seems only valid for the first laser pulse. During and after the etching laser pulse subsequent processes such as decomposition of the liquid, the formation of a bubble and its interaction with the solid surface, and the resolidification of a thin molten layer of the sample cause the modification of a near surface region of the material. Consequently, for a multi-pulse irradiation employing UV ns pulses and organic absorbing liquids, the discussion of the etch mechanism has to be improved by a highly absorbing layer at the interface between solid and liquid.

The properties and the thickness of this modified layer alter during the prolonged etching process. Basically, it can be distinguished between incubation pulses and the steady state etching situation whereas a transition period can be expected, too. The period of incubation pulses is characterized by the deposition of a carbon layer (decomposition products from the liquid). When the absorbance is large enough, the etching starts. Now, the near surface region of the sample is damaged due to the melting and fast resolidification of a thin material layer and the etching process is in the steady state. The deposited layer is important for the beginning materials erosion but the etching process itself and consequently  $\Delta h$  is probably triggered by the process of structural damaging of the near surface region of the solid sample due the large temperatures (and probably pressure). Thus, there probably exists a positive feedback between the processes of surface modification and etching.

Customarily, the melting temperature is proposed as the critical temperature for starting materials erosion [8, 72, 73]. In this presented work, the validity  $T_c = T_M$  (in the case of vitreous fused silica  $T_M$  of cristobalite) is not unambiguously substantiated by the calculations of the interface temperature in section 8.2. In fact, the computations show that the point of beginning vaporizing of SiO<sub>2</sub> melt ( $T_B = 2900^{\circ}$ C) seems more probably as  $T_c$  than the melting temperature.

No evidence like resolidified ridges at the edge of etched area for a viscous flow of the heated material due to a large-pressure impact of the heated liquid is found during the experiments. The calculated temperatures at the interface can exceed 4000°C within 25 ns also for small fluences. Thus, a materials overheating beyond the temperature of vaporization is possible and fast and explosive evaporation takes place. In this case, the dominating mechanism for multi-pulse irradiation of LIBWE is probably the ablation of the modified back surface due to an effective absorption of the laser energy by a highly absorbing interface layer.
# 9 Applications for microstructuring with LIBWE

The knowledge of the influence of processing parameters on etching and contributing mechanisms is of fundamental importance to apply LIBWE for high-end applications in microoptics or microfluidics. Based on the results (chapter 5 and 6) a parameter window for optimized surface quality can be defined in the case of fused silica and pyrene in toluene solutions: (i) the pyrene molarity should be at least 0.3 M; (ii) the etch rates must be limited to a range extending from 5 to 15 nm/pulse; and (iii) the final etch depth should not distinctly exceed 20  $\mu$ m to guarantee a sufficient surface quality. This can be reached usually with fluences in the middle fluence region but the etch rates depend at a fixed fluence on the chosen size of irradiated area, too. Additionally, since incubation influences the LIBWE process distinctly (section 7.1), the pulse number necessary for a certain depth must include the pulse number to overcome the incubation (incubation pulses) and the pulse number to achieve the desired etch depth.

To demonstrate the capabilities of LIBWE, the fabrication of surface features applicable in microoptics with both binary and analogous depth profiles is shown applying suitable laser techniques for microstructuring (see section 4.2). The achieved structure widths range extending from a few hundred micrometers to half of a micron whereas the etch depth can be adjusted between a few ten nanometers and 20 micrometers. After processing, the samples are cleaned by the gentle oxygen plasma etch process (4.4.2) to remove the modified near surface region of the fused silica samples. Measurements of the transmittance are carried out and show that no difference between etched and unetched fused silica exists.

# 9.1 Binary structures

#### 9.1.1 Multi-stepped binary element

To verify the processing parameters and to examine the reproducibility of the laser etching, test structures are etched into fused silica. Fig. 9-1 shows an etched binary structure measured by interference microscopy. The footprint of a single element is set to  $(30 \cdot 30) \mu m^2$ . The large reproducibility of the etching is demonstrated in the rows with the same applied pulse numbers (R3–R6). In other rows (R1, R2, R7, R8) multi-step topographies are machined with different pulse numbers. The



Fig. 9-1: WLIM image of laser-machined multi-stepped binary elements etched into fused silica at a laser fluence of 0.90 J/cm<sup>2</sup> with  $A_s = (30 \cdot 30) \,\mu\text{m}^2$ . In the rows 3 to 6 etching is processed with a constant pulse number of 30, 50, 70, and 80 pulses, respectively. In the other rows multi-stepped topographies are etched with increasing pulse numbers. Rows 1, 7, and 8 starts with 10 laser pulses and the etch depths increase with an increment of 5 (R1 and 7) and 10 (R8) pulses.

etched pits feature a slightly convex bottom that is not caused by energy density distribution of the laser beam. The reasons for this surface features are not known yet. However, this curved bottom appears also very reproducible so that this can be taken into account into the calculations of diffractive elements. Moreover, with gray scale masks instead of square contour masks an appropriate laser fluence distribution can be adjusted in this way that an almost flat etched bottom results.

#### 9.1.2 Fabrication of stepped phase gratings

Both reflection and transmission line gratings are widely used for optical applications. Especially transparent phase gratings can be used for laser applications, such as beam splitters, phase masks, or gray scale masks [2]. Phase masks with a binary rectangular profile are fabricated for these applications by standard lithographic methods.

LIBWE in conjunction with scanning small spot technique (section 4.2) is exploited for the fabrication of a phase grating to demonstrate the capabilities of direct laser etching for machining binary optics. The grating properties, such as grating profile, line-space ratio, and depth, can be adjusted to the application by the selection of an appropriate mask and suitable processing parameters. Fig. 9-2 shows a SEM image



Fig. 9-2: SEM image of an etched phase grating with a period of  $22 \,\mu\text{m}$  and an etch depth of 350 nm. The patterning is achieved by scanning a rectangular mask across the surface.

of a grating etched in fused silica by means of small spot scanning. The phase grating is fabricated at a fluence of 0.90 J/cm<sup>2</sup> by means of an  $(11 \cdot 50) \mu m^2$  rectangular mask. According to the used mask the grating period is about 22  $\mu m$  with a linespace ratio of one. The etched grating grooves have a uniform depth of 350 nm with an estimated roughness of less than 2 nm rms. The SEM micrograph of the etched grating additionally confirms the very good surface quality (no texture, continuous transition between the pulses) and the small roughness.

## 9.1.3 Submicron gratings

By means of projecting a transmission phase grating with a Schwarzschild objective (see section 4.2) a periodical fluence distribution is generated onto the back surface of the fused silica sample and gratings with a period obeying to the theory are etched [77].

Fig. 9-3a presents a SEM image of a sinusoidal line grating (1D) etched with 10 pulses at a laser fluence of 1.30 J/cm<sup>2</sup>. The grating depth and period are estimated by AFM measurements to be about 120 and 760 nm, respectively. The period of the etched gratings depends on the used optical set-up for phase mask projection, the grating period of projected phase grating, and the demagnification provided by the imaging objective (see section 4.2). The angle of the two interfering laser beams can be calculated from the diffraction angle after the phase grating given by  $\lambda/a$  and the magnification of projection optics. By means of a phase mask with a grating period of 22 µm and an objective having a demagnification of 15x a line spacing of 730 nm can be calculated. This is in good agreement with the measured 760 nm



Fig. 9-3: a) SEM image of a 1D grating etched by projecting a line phase mask onto the fused silica back surface. The cross section in the inset well describes the sinusoidal profile with the 760 nm period as result of the intensity distribution due to the interfering beam lets. b) AFM image of etched 2D patterns wit a period of about 550 nm by projection of a chessboard-like phase mask.

grating period. The difference presumably arises from the influence of the sample thickness, which is part of the optical beam path.

Beside line gratings also 2D gratings can be easily fabricated by exchanging line grating phase mask against chessboard-like phase mask. As result of the projection of such a mask well and regularly ordered dot pattern can be achieved as the AFM image in Fig. 9-3b depicts. The period and depth of the structure is estimated to be 550 nm and 80 nm, respectively.

Generally, after etching the fabricated surface features two main characteristics, the development of expected surface gratings and a homogeneous material etching over the entire illuminated area, further called *over-all-etching* (OAE) [77]. The laser fluence and the pulse number influence both the grating depth as well as the OAE depth. The evolution of etched grating profile from deep, acute-angled grooves to sinusoidal relief and the decrease of the grating depth with increasing laser fluence is described elsewhere [77].

In addition, LIBWE of sub-micron sinusoidal relief gratings by projection of transmission phase masks shows a limitation in grating depth with increasing pulse number whereas the OAE-depth increases linearly. Therefore, the etch rates, which are similar at the peaks and the valleys at larger pulse numbers, disagree with the fluence distribution of the interfering laser beams. Moreover, over-etching of sinusoidal relief gratings (period 760 nm) with a homogeneous distributed laser beam causes vanishing of the grating with increasing pulse number, which is related to a proposed LIBWE inherent smoothing effect [78].

## 9.2 Analogous/curved structures

#### 9.2.1 Microprism array and microlens

Fig. 9-4 illustrates a microprism array in fused silica with a period of 24  $\mu$ m and a final depth of 900 nm and a microlens with a depth of about 10  $\mu$ m. Here the scanning contour mask technique is applied that makes use of special designed masks whose contour corresponds to the desired profile. The inset in Fig. 9-4a shows the cross section of the etched microprism structure measured by AFM. Additionally to the plane and smooth surfaces and sharp edges of etched prisms the etched surface roughness is below 5 nm rms that complies the quality of technical optics. The prism is etched by line scanning of a triangle mask (equilateral) with a side length of 30  $\mu$ m. The laser fluence, pulse repetition rate, and scan velocity are set to 1.00 J/cm<sup>2</sup>, 100 Hz, and 30  $\mu$ m/s, respectively. Large arrays of the microprisms are achieved by adjoining of single line scans with a virtual overlap of 6  $\mu$ m. The microlens (Fig. 9-4b) is fabricated by a single scan of a semicircle mask with a radius of 200  $\mu$ m. The microroughness of concave cylindrical structure is below 10 nm rms at an etch depth of about 10  $\mu$ m.

#### 9.2.2 Phase grating to homogenize a laser beam

Beside beam splitting applications (see subsection 9.1.2) special designed laser etched gratings can be used as laser beam homogenizing optics for high power applications. Such phase masks feature large laser damage threshold and allow the application of low demagnification optics. For demonstration of the capabilities of direct laser machining with LIBWE a phase grating for homogenizing a Gaussian shaped HeNe laser beam is etched. The depth of the grating is calculated consider-



Fig. 9-4: SEM image of analogous/curved structures etched by scanning a contour mask. a) Microprism array in fused silica featuring sharp edges and smooth surfaces. The inset presents a cross section measured by AFM. b) A microlens etched by single scan of a semicircle mask.

ing wavelength and measured laser intensity distribution of the HeNe laser beam.

The grating structures are written into the surface with a rectangular mask of  $(15 \cdot 50) \ \mu\text{m}^2$ . The different depths of the grating grooves can be achieved by varying the scan velocity of the mask. The velocities are calculated on the base of mask size, used processing parameters, and local depth of the grating that is required to realize the optical function. The phase grating etched by this method features a depth distribution in the range of 0-350 nm to cause an equivalent phase shift.



Fig. 9-5: a) Depth of etched grating in comparison to the calculated profile. b) Intensity distribution of a HeNe laser beam homogenized with the grating microoptic in comparison to the original laser beam.

Thus, the diffraction of the grating can be adjusted locally. The measured depths across the center of laser-etched grating are depicted in Fig. 9-5a in comparison to the calculated depth distribution. The depth of the grating grooves coincides with the calculated depth distribution well. The roughness of the groove bottom is about 3 nm rms. The optical functionality of the laser-written phase grating is studied by means of a HeNe laser beam. The laser intensity of the HeNe laser beam measured by CCD camera with and without beam shaping diffraction grating is shown in Fig. 9-5b. The original Gaussian intensity distribution. Other laser beam properties, e.g., the divergence, are basically not changed by the diffraction grating. Furthermore, other designs of gratings result in further shapes of the laser beam, e.g., annular profile [80].

## 9.2.3 Asphere

Patterning large areas with repetitive elements may be achieved by a step-andrepeat as well as with scanning processes. In the case of processing large areas with small spot laser techniques, the adjacent laser processed areas must be fit to achieve smooth etched surface at extended areas. Quadratic masks should give perfect surfaces but inaccuracies of the work piece handling system and real-world physical effects, such as scattering of the laser beam at edges of the previously machined structure, result in narrow trenches or ridges. A much better surface quality and a larger tolerance to machining inaccuracies associated with the laser processing can be expected for a scanned rhombic masks [143]. Consequently, to make use of the flexibility of the laser beam and to achieve sufficient lateral resolution a small homogenously illuminated rhombic mask with a side length of 70  $\mu$ m is selected for etching free-form elements with nanometer depth resolution into a plane fused silica substrate by means of LIBWE (Fig. 9-6a).

However, as known from [4] the depth of 3D-topographies, which are processed by means of the scanning contour mask, is controlled by the number of locally applied laser pulses. Hence, incubation effects have to be considered. One result of incubation effect on the etch process with the scanning rhombic-sized small spot mask is the lower width of the etched tracks in comparison with the diagonal of the mask. Hence, the distance of the adjacent scans has to be optimized. To achieve different etch depths the scanning velocities of the mask are calculated on base of the etch



depth taking into account the incubation processes.

To demonstrate the capabilities of the direct laser processing a free-form surface has been etched with nanometer depth precision (Fig. 9-6a). As processing parameter a fluence of 1.00 J/cm<sup>2</sup> and a (70 · 70)  $\mu$ m<sup>2</sup> rhombic mask are applied. From the given target surface, a saddle function according to  $z(r, \varphi) = r^2 \sin(2\varphi)$  with a final depth of  $z_{max} = 500$  nm (Fig. 9-6b), the velocity distribution of the laser beam is calculated. Such very shallow refractive elements can be used, e.g., for wave front correcting of optical elements. The etched surface measured by interference microscope as well as respective cross sections corresponding to the dashed lines are depicted in Fig. 9-6a and c and represent the target surface very well. The maximal depth of the free-form surface has been attainted with a deviation of less than 10%. The surface roughness measured optically within small areas is as small as 10 nm rms. The surface quality can be further improved with specific designed masks with gray scale features, by enhancing the homogeneity of the used laser beam, and by optimization of the processing parameters.

# **10** Summary and concluding remarks

The laser-induced backside wet etching (LIBWE) is a promising technique for direct patterning of transparent materials with high quality. In this work the etch process has been experimentally investigated to study the etch mechanism and ascertain the dominating processes. Therefore, correlations between the model and the experimental results have been drawn.

At first the influence of process parameters and processes on the etch rate and the surface quality have been systematically studied for LIBWE with organic solutions employing an excimer laser with nanosecond pulses. In particular, the effects of laser fluence, pulse number, spot size, pulse repetition rate, laser wavelength, absorbing organic liquid, and the kind of the transparent material on the etching have been determined. The main characteristics of the etching process are a specific etching threshold, a certain etch efficiency, an incubation behavior, and a surface microtopography that depend on the etched material and the used solution.

The surface quality of fused silica has been investigated in detail by means of white light interference microscopy, SEM, and AFM to study the figure, the waviness, and the roughness of the etched surface. To characterize the chemical and physical properties of the etched surface, Raman spectroscopy, XPS, and RBS/channeling measurements are performed. Additionally, in situ reflection measurements and UV/VIS transmission spectroscopy have been carried out. These results have shown that a near surface region suffers from chemical and structural modifications that cause the alteration of the materials absorbance also at the used laser wavelengths. The irradiated liquid has been analyzed by means of GC-MS, Raman spectroscopy, SEM, and TEM. These results indicate to specific decomposition processes causing the formation of carbon products or even carbon.

Concluding from the experimental results, an optimized parameter window for high-quality surface processing of fused silica is proposed: (i) pyrene in toluene solutions with molarity of at least 0.3 M; (ii) etch depth per pulse limited to a range from 5 to 20 nm/pulse; (iii) pulse number per place exceeding 30 to 50 pulses to overcome incubation effects and achieve steady state etching, and (iv) final etch depths from 200 nm to 20  $\mu$ m. This can be reached with laser fluences in the range from 0.60 to 1.20 J/cm<sup>2</sup> but also depends on the size of the irradiated area.

The currently discussed mechanism of LIBWE cannot sufficiently interpret the experimental results and is unable to explain LIBWE-related processes such as incubation, liquid decomposition, and surface modification. Based on correlations of the experimental results and physical models of selected processes, the dominating processes are discussed and an improved model of LIBWE has been developed. The main improvement of the model is the introduction of a layer at the interface between the solid and the liquid with altered materials properties. In particular, the layer offers a large absorbance for the incident laser radiation and therefore distinctly affects the possible temperatures at the solid-liquid interface. Based on the improved etching model and the results from surface analytical measurements, the computed temperatures at the interface far exceed the boiling point of the solid. Recapitulating the influence of liquids decomposition and surface modification on the etch behavior and the temperature modeling materials erosion in LIBWE follows a liquid-induced backside ablation mechanism.

The fabrication of well-defined and high quality surface features into transparent dielectrics, such as fused silica, by LIBWE is demonstrated. With organic solvents and solutions as absorbing liquids, materials erosion takes place at laser fluences that are more than one order of magnitude smaller than those required for direct laser ablation in air. Depending on the applied laser processing technique, the etched surfaces feature stepped binary elements, analogous smooth curvatures, and regular periodic structures with a lateral resolution smaller than  $1\mu m$ , which are potentially applicable for the shaping of microoptical components.

With the experimental results and the improved etch model, basic tools for the further optimization of the process and a more accurate control of the process parameters are now available and enable new developments for industrial applications of this promising etching technique.

# **11 Outlook**

Further developments related to LIBWE should comprise at least the following main topics: (i) Further investigations of the laser-liquid-induced modification of the near surface layer of the solid material. (ii) The improvement of the thermal model of LIBWE considering additional processes such as melting and vaporization, temperature dependent material properties, and graded absorption near the surface. Furthermore, the current 1D temperature model has to be extended to a 3D model. (iii) The extension of the etching technique with regards to new materials and industrial lasers using the metallic liquid approach. (iv) The development of industrial technologies that utilizes the scientific findings to apply the LIBWE technique for the etching of pattern for microfluidics and microoptics.

In detail, time-resolved in situ measurements of the reflectance and transmittance (pump probe set-up) during the duration of the laser pulse together with emission spectroscopy will be necessary. Furthermore, studies with spectroscopic ellipsometry and SIMS (secondary ion mass spectroscopy) are planned to determine more precisely the properties of the modified layer, e.g., the thickness and absorption coefficient, to facilitate analytical interpretations and yield more precise parameters for numerical simulations of laser-induced backside wet etching.

The presented analytical temperature model has to be upgraded with an analytical solution for the liquid volume heat by implementation of a proper heat transition function. In a further step, numerical simulations with finite element method (FEM) program code concerning phase transitions and temperature-dependent materials properties have to be carried out to derive models of the dynamic thermal processes involved in etching with more quantitative and numerical explicitness. The simulations must consider the cooling cycle to gain information or evidence about the depth of heated material as well as the point in time for material erosion.

# Appendices

Parameters	Symbol	Value
Refractive index	n	1.51 (λ = 248 nm)
		1.45 ( $\lambda$ = 820 nm)
Density	Q	2.20 g/cm <sup>3</sup>
Specific heat capacity	$C_p$	0.70 J/(gK)
Thermal conductivity	К	1.38 W/(mK)
Coefficient of thermal expansion	ß	5.5 · 10 <sup>-7</sup> K <sup>-1</sup>
Thermal diffusivity	D	$9.49 \cdot 10^{-3}  \text{cm}^2/\text{s}$
Glass transition point of fused silica	$T_g$	1200°C [41]
Melting temperature of cristobalite	$T_M$	1720°C [17, 41, 47]
Temperature of beginning evaporation of		
SiO <sub>2</sub>	$T_B$	2900°C [43]
Compressive strength		1100 MPa
Tensile strength		50 MPa

 Table A 1: Properties of fused silica at room temperature [144]

Parameters	Symbol	Value
Molar mass	М	92.14 g/mol
Density	Q	$0.87 \text{ g/cm}^3$
Refractive index	n	1.60 ( $\lambda$ = 248 nm) [145] (estimated from refractive index dispersion formula)
		1.49 ( $\lambda$ = 820 nm) [145]
Boiling temperature	$T_B$	110°C
Specific heat capacity	Cp	1.71 J/(gK)
Thermal conductivity	K	0.13 W/(mK)
Thermal diffusivity	D	$0.87 \cdot 10^{-3}  \mathrm{cm}^2/\mathrm{s}$
Coefficient of thermal expansion	β	100 · 10 <sup>-5</sup> K <sup>-1</sup>
Sound velocity	, Cs	13.2 · 10 <sup>4</sup> cm/s
Critical temperature (supercritical fluid)		319°C [146]
Critical pressure (supercritical fluid)		41 bar [146]

Liquids	Molar mass	Boiling tempera-	Density	Specific heat capacity	Thermal diffusivity	Sound ve- locity
	M (g/mol)	(°C)	<i>Q</i> (g/cm³)	с <sub>р</sub> (J/(g K))	D (10 <sup>-3</sup> cm <sup>2</sup> /s)	<i>c</i> s (10 <sup>4</sup> cm/s)
Acetone (C3H6O)	58.08	56.2	0.79	2.16	0.96	11.7
$\begin{array}{c} \text{(C_{3}\text{H}_{10})} \\ \text{(C_{8}\text{H}_{10})} \end{array}$	106.17	139	0.87	1.71	0.87	13.4
Acethylacetone	100.12	140	0.96	2.08	NA	13.8
Chlorobenzene	112.56	130	1.02	1.35	0.87	12.9
Dichloroben-	147.00	180	1.30	1.16	0.70	12.3
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	96.10	85	1.11	1.52	NA	NA

Table A 3: Selected properties of used liquids at room temperature

Table A 4: Selected physical properties of used transparent solids [144] at room temperature

Glass transi- tion <sup>i</sup> or mel- ting <sup>ii</sup> tempe- rature (°C)	Density Q (g/cm <sup>3</sup> )	Specific heat capacity c <sub>p</sub> (J/(gK))	Coefficient of thermal expansion $\beta$ $(10^{-7} \text{ K}^{-1})$	Thermal conductivity κ (W/(mK))	Thermal diffusivity D (10 <sup>-3</sup> cm <sup>2</sup> /s)
719 <sup>i</sup>	2 5 1	0.82	72	0.92	4 5
/1/	2.51	0.02	72	0.72	1.5
736 <sup>i</sup>	2.51	0.86	83	1.11	5.2
719 <sup>i</sup>	2.23	0.75	32.5	1.1	6.54
821 <sup>i</sup>	2.76	NA	46	NA	NA
1720 <sup>ii</sup>	2.64	0.71	80 (o) 124 (aa)	10.7(0)	57
2050 <sup>ii</sup>	3.98	0.75	134 (a0) 53 (0) 45 (aa)	6.2 (ab) 40	133
1528 <sup>ii</sup>	3.18	1.01	45 (a0) 140 (0) 85 (ap)	21	66
1420 <sup>ii</sup>	3.18	0.85	188 (o)	9.71	36
	Glass transi- tion <sup>i</sup> or mel- ting <sup>ii</sup> tempe- rature (°C) 719 <sup>i</sup> 736 <sup>i</sup> 719 <sup>i</sup> 821 <sup>i</sup> 821 <sup>i</sup> 1720 <sup>ii</sup> 2050 <sup>ii</sup> 1528 <sup>ii</sup> 1420 <sup>ii</sup>	Glass transi- tioni or mel- tingii tempe- rature (°C)       Density (°C)         719i       2.51         736i       2.51         719i       2.23         821i       2.76         1720ii       2.64         2050ii       3.98         1528ii       3.18         1420ii       3.18	Glass transi- tioni or mel- tingii tempe- rature $\varrho$ (°C)Specific heat capacity $\varrho$ (J/(g K))719i2.510.82736i2.510.86719i2.230.75821i2.76NA1720ii2.640.712050ii3.980.751528ii3.181.011420ii3.180.85	Glass transi- tioni or mel- tingii tempe- rature (°C)Density $\varrho$ (g/cm3)Specific heat capacity $\zeta_p$ (J/(g K))Coefficient of thermal expansion $\beta$ (10-7 K-1)719i2.510.8272736i2.510.8683719i2.230.7532.5821i2.76NA461720ii2.640.7180 (o) 134 (ao) 2050ii13.181528ii3.181.01140 (o) 85 (ao) 188 (o)	Glass transi- tioni or mel- rature (°C)Density $\rho$ (g/cm3)Specific heat capacity $\rho$ (J/(gK))Coefficient of thermal (main of thermal) $\beta$ (10-7 K-1)Thermal conductivity expansion $\beta$ (W/(mK))719i2.510.82720.92736i2.510.86831.11719i2.230.7532.51.1821i2.76NA46NA1720ii2.640.7180 (o) 134 (ao) 45 (ao)10.7 (o) 6.2 (ao) 40 45 (ao)1528ii3.181.01140 (o) 85 (ao) 188 (o)21 85 (ao) 9.71

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# List of own publications, patents, and awards

The following articles, posters, and lectures have been published in the course of this theses, are submitted, or in preparation for future publication.

### Articles in peer-reviewed scientific journals

Publications on backside etching:

- 1. R. Böhme, A. Braun, K. Zimmer: "Backside etching of UV-transparent materials at the interface to liquids" Appl. Surf. Sci. **186**, 1-4 (2002) 276-281.
- K. Zimmer, R. Böhme, A. Braun, B. Rauschenbach, F. Bigl: "Excimer laser-induced etching of submicron surface relief gratings in fused silica using phase grating projection" Appl. Phys. A 74, 4 (2002) 453-456.
- 3. K. Zimmer, A. Braun, R. Böhme: "Etching of fused silica and glass with excimer laser at 351 nm" Appl. Surf. Sci. **208** (2003) 199-204.
- 4. R. Böhme, D. Spemann, K. Zimmer: "Surface characterization of backside-etched transparent dielectrics" Thin Solid Films **453-454** (2004) 127-132.
- 5. K. Zimmer, R. Böhme, B. Rauschenbach: "Laser etching of fused silica using an adsorbed toluene layer" Appl. Phys. A **79** (2004), 1883-1885.
- 6. R. Böhme, K. Zimmer: "Low roughness laser etching of fused silica using an adsorbed layer" Appl. Surf. Sci. **239** (2004), 109-116.
- R. Böhme, J. Zajadacz, K. Zimmer, B. Rauschenbach: "Topography and roughness evolution of microstructured surfaces at laser-induced backside wet etching" Appl. Phys. A, 80 (2005) 433-438.
- K. Zimmer, R. Böhme: "Precise etching of fused silica for micro optical applications." Appl. Surf. Sci. 243, 1-4 (2005) 417-422.
- 9. K. Zimmer, R. Böhme, B. Rauschenbach: "Adsorbed layer etching of fused silica by excimer laser with nanometer depth precision" Microelectron. Eng. **78-79** (2005) 324-330.
- 10. R. Böhme and K. Zimmer: "The influence of the laser spot size and the pulse number on backside wet etching" Appl. Surf. Sci. **247** (2005) 256-261.
- 11. K. Zimmer, R. Böhme: "Precise etching of fused silica for refractive and diffractive micro optical applications" Opt. Laser. Eng. **43**, 12 (2005) 1349-1360.
- 12. R. Böhme, K. Zimmer, B. Rauschenbach: "Laser backside etching of fused silica due to carbon layer ablation" Appl. Phys. A **82**, 2 (2006) 325-328.
- 13. R. Böhme, K. Zimmer: "Effects of halogenated organic solvents at laser-induced backside wet etching" Appl. Phys. A **83** (2006), 9-12.
- 14. R. Böhme, S. Pissadakis, M. Ehrhardt, D. Ruthe, K. Zimmer: "Ultra-short laser processing of transparent material at the interface to liquid" J. Phys. D **39** (2006), 1398-1404.
- 15. R. Böhme, D. Hirsch, K. Zimmer: "Laser etching of transparent materials at a backside surface adsorbed layer" Appl. Surf. Sci. **252** (2006), 4763-4767.
- 16. R. Böhme, T. Otto, K. Zimmer: "In situ reflectance investigations of solid-liquid interface during laser backside etching" Appl. Surf. Sci. **252** (2006), 4392-4396.
- 17. K. Zimmer, R. Böhme, D. Ruthe, B. Rauschenbach: "Backside laser etching of fused silica using liquid gallium" Appl. Phys. A **84** (2006), 455-458.
- 18. R. Böhme, S. Pissadakis, D. Ruthe, and K. Zimmer: "Laser backside etching of fused silica with ultra-short pulses" Appl. Phys. A **85** (2006), 75-78.
- 19. K. Zimmer, R. Böhme, D. Hirsch, B. Rauschenbach: "Backside etching of fused silica with UV-ns laser pulses using mercury" J. Phys. D **39** (2006) 4651-4655.
- 20. K. Zimmer, R. Böhme, S. Pissadakis, L. Hartwig, G. Reisse, B. Rauschenbach: "Backside etching of

fused silica with Nd:YAG laser" Appl. Surf. Sci. 253 (2006) 2796-2800.

- 21. K. Zimmer, R. Böhme, B. Rauschenbach: "Using IR laser radiation for backside etching of fused silica" Appl. Phys. A, **86** (2007) 409-414.
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- 23. K. Zimmer, R. Böhme, B. Rauschenbach: "Enhancing the etch rate at backside etching of fused silica" Journal of Laser Micro/Nanoengineering, **1**, 3 (2006) 292-296.
- 24. R. Böhme, S. Pissadakis, M. Ehrhardt, T. Rudolph, D. Ruthe, K. Zimmer: "Backside etching of fused silica with ultra-short laser pulses at the interface to absorbing liquid" J. Phys. D, accepted for publication.
- 25. R. Böhme, K. Zimmer: "Indirect laser microstructuring of fused silica: from nanometer to high rate processing" Appl. Surf. Sci., accepted for publication.
- 26. K. Zimmer, R. Böhme, D. Ruthe, B. Rauschenbach: "The influence of laser-induced surface modifications on the backside etching process" Appl. Surf. Sci., accepted for publication.
- 27. S. Pissadakis, R. Böhme, K. Zimmer: "Sub-micron periodic structuring of sapphire crystal by LIBWE" Optics Express, accepted for publication.
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#### Publications on other subjects:

- T. Höche, R. Böhme, J. W. Gerlach, F. Frost, K. Zimmer, B. Rauschenbach: "Semiconductor Nanowires Prepared by Diffraction-Mask-Projection Excimer-Laser Patterning" Nanoletters 4, 5 (2004) 895-897.
- 30. T. Höche, R. Böhme, J. W. Gerlach, B. Rauschenbach: "Nanoscale laser patterning of thin gold films" Philos. Mag. Lett. **86**, 10 (2006), 661-667.
- 31. K. Zimmer, R. Böhme, D. Ruthe, T. Rudolph, B. Rauschenbach: "Local growth of vertical aligned carbon nanotubes by laser-induced surface modification of coated silicon substrates" J. Phys. D, accepted for publication.
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- 34. D. Ruthe, K. Zimmer, R. Böhme and B. Rauschenbach: "Up- and down-trimming of thick film resistors by ultrashort pulse laser irradiation" Journal of Laser Micro/Nanoengineering, accepted for publication.

#### Articles in journals and conference proceedings without reviewing

- 35. A. Braun, K. Zimmer, R. Böhme: "Anwendungsbeispiele zur Oberflächenbearbeitung mittels Excimerlaser" Proc. 14th International Scientific Conference, Mittweida (2000).
- 36. R. Ebert, R. Böhme, S. Klötzer, P. Regenfuß, B. Keiper, G. Reiße, H. Exner: "Lasermikrobearbeitung im Vakuum" Lasermagazin 6 (2001) 22.
- 37. K. Zimmer, R. Böhme, A. Braun: "Microstructuring of dielectrics by laser-induced back side etching" Proc. 3rd International Conference and 4th General Meeting of EUSPEN, Eindhoven (2002).
- 38. R. Böhme, K. Zimmer: "Präzisionsbearbeitung transparenter Materialien mit dem Excimerlaser" Lasermagazin 4 (2002) 25-28.
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- 40. R. Böhme, K. Zimmer: "Laserrückseitenätzen mit Excimerlasern eine Methode zur präzisen

Mikrostrukturierung von Quarz und optischen Gläsern" Photonik 2 (2003) 70-73.

- 41. R. Böhme, K. Zimmer: "Direct laser etching of high quality microstructures in Pyrex for applications in micro-system technology" Proc. Microsystem Technologies, München (2003) 242-247.
- 42. K. Zimmer, R. Böhme: "Ultra-Präzise Bearbeitung von Oberflächen mit Pulslasern" Proc. IWKM, Mittweida (2003).
- R. Böhme, K. Zimmer: "Charakterisierung von LIBWE-geätzten Oberflächenstrukturen in Quarz" Proc. IWKM, Mittweida (2003).
- 44. B. Keiper, R. Ebert, R. Böhme, H. Exner: "Microstructuring of PYREX glass and polymers by excimer laser" Proc. Smart Sensors, Actuators, and MEMS, Maspalomas, Gran Canaria, Spain, SPIE, 5116 (2003) 20-27.
- 45. R. Böhme, K. Zimmer: "Rapid Prototyping von diffraktiven und refraktiven mikrooptischen Elementen" Photonik 3 (2004) 58-61.
- 46. R. Böhme, K. Zimmer: "Direct laser etching of optical glasses for flexible fabrication of microoptical structures" Proc. OPTO Kongress, Nürnberg (2004) 25-31.
- 47. K. Zimmer, R. Böhme: "Laser Etching of Fused Silica for Diffractive and Refractive Optics" Proc. MOC'04, Jena (2004).
- R. Böhme, K. Zimmer: "Laser Backside Etching of Transparent Material for the Fabrication of Diffractive and Refractive Topographic Features" Proc. Microsystem Technologies, München (2005) 63-70.
- 49. R. Böhme, K. Zimmer: "Ultraglatt und hochpräzise: Laserabtrag an der Rückseite transparenter Dielektrika" Photonik 1 (2006) 50-52.
- 50. R. Böhme, K. Zimmer, B. Rauschenbach, "Direct laser etching of transparent materials: High quality surface patterning and figuring for micro-optical applications" Proc. SPIE 6254 (2006) 203-211.
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- 53. D. Ruthe, K. Zimmer, R. Böhme, B. Rauschenbach: "Strukturierung und Modifizierung dünner Schichten mit ultrakurzen Pulsen für elektronische Anwendungen" Proc. IWKM, Mittweida (2006).
- 54. R. Böhme and K. Zimmer: "Smooth and precise: laser etching at the backside of transparent dielectrics" Photonik International 2006, in progress.

#### **Posters presentations**

- 1. "Microstructuring of dielectrics by laser-induced back side etching" 3rd International Conference and 4<sup>th</sup> General Meeting of EUSPEN, Eindhoven (2002).
- 2. "Surface characterization of backside-etched transparent dielectrics" EMRS, Strasbourg (2003).
- "3D-microstructuring of Pyrex glass for the manufacturing of hybrid microsystems by laser processing" SENSOR Kongress, Nürnberg (2003).
- 4. "Laser fabrication of micro sized diffractive and refractive optical devices in fused silica and glass" LASER 2003, CLEO, München (2003).
- 5. "Etching of fused silica by excimer laser with nanometer depth precision" MNE 2004, Rotterdam (2004).
- 6. "Laser Etching of Fused Silica for Diffractive and Refractive Optics" MOC'04, Jena (2004).
- "Laser etching of transparent materials at a backside surface adsorbed layer" EMRS, Strasburg (2005).
- "Backside etching of fused silica with ultra-short laser pulses at the interface to absorbing liquid" COLA 2005, Banff (Canada) (2005).

9. "Surface investigations of fused silica surfaces etched by laser etching at a surface adsorbed layer (LESAL)" ICPEA, Charlottesville (USA), 03.-07.09. (2006).

# **Oral presentations**

- 1. "Direct laser etching of high quality microstructures in Pyrex for applications in micro-system technology" Microsystem Technologies, München (2003).
- 2. "Charakterisierung von LIBWE-geätzten Oberflächenstrukturen in Quarz" IWKM, Mittweida (2003).
- 3. "Direct laser etching of optical glasses for flexible fabrication of micro-optical structures" OPTO Kongress, Nürnberg (2004).
- 4. "LIBWE: laser-induced backside wet etching of transparent materials" Lecture at Institute of Electronic Structure and Laser (IESL), Heraklion (Greece) (2004).
- 5. "In situ reflectance investigations of solid-liquid interface during laser backside etching" EMRS, Strasburg (France), 31.05.-03.06. (2005).
- 6. "Direct laser etching of transparent materials: High quality surface patterning and figuring for micro-optical applications" Seventh International Conference "Correlation Optics", SPIE, Chernivtsi (Ukraine), 06.-09.09. (2005), (invited talk).
- 7. "Laser Backside Etching of Transparent Material for the Fabrication of Diffractive and Refractive Topographic Features" Microsystem Technologies, München, 05.-06.10. (2005).
- 8. "Laser etching of periodic 1D- and 2D submicron relief gratings on pre-structured fused silica surface" Photonics Europe, SPIE, Strasbourg (France), 03.-07.04. (2006).
- 9. "Backside etching at the interface to diluted medium with nanometer etch rates" 4th International Congress on Laser Advanced Material Processing, LAMP2006, Kyoto (Japan), 16.05. -19.5. (2006).
- 10. "Indirect laser microstructuring of fused silica: from nanometer to high rate processing" EMRS, Nice (France), 29.05.-02.06. (2006).
- 11. "Laserätzen an der Rückseite transparenter Materialien Stand und weitere Entwicklungen" IWKM, Mittweida, 09.-11.11. (2006).

# Patents

- 1. R. Böhme, K. Zimmer: "Vorrichtung und Verfahren zum Laserabtrag transparenter Materialien" Patent Granted Germany DE10328534.
- 2. K. Zimmer, R. Böhme: "Verfahren zur Präzisionsbearbeitung von transparenten Materialien mit gepulster Laserstrahlung" Patent Granted Germany DE10328559.
- 3. K. Zimmer, R. Böhme: "Verfahren zum Abtrag von lichtdurchlässigen Materialien mit Laserstrahlung und Vorrichtung hierfür" Patent Application Germany 10 2005 055 174.2 (18.11.2005).

## Awards

Best Poster Award, Symposium J: "Advantages in Laser and Lamp Processing of Functional Materials", EMRS, Strasburg (France), 31.05.-03.06. (2005).

Young Scientist Award of the European Materials Research Society for the work on laserinduced backside wet etching of transparent dielectric materials, EMRS, Nice (France), 29.05.-02.06. (2006).

# Curriculum vitae

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Army service:				
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Study:				
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02/2001	Diploma thesis, "Untersuchungen zum laserinduzierten Flüssigkeits-Rückseitenätzen von UV-transparenten Mate- rialien mit dem Excimerlaser" at the Leibniz-Institut für Oberflächenmodifizierung e.V., Leipzig			
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03/2001 - 05/2001	Scientific employee at the Leibniz-Institut für Oberflächen- modifizierung e.V., Leipzig			
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# Statement

I certify that this thesis is based on my own work. I also certify that - to the best of my knowledge - any help received in preparing this work, and all sources used, have been acknowledged in this thesis. Furthermore I certify, that I did not submit this or any other thesis to attain PhD degree to another technical university, academia, or university to this day.

Leipzig, 31 January 2007

Rico Böhme