Digital Photonic Production of Corundum Components by SLE

Digitale photonische Produktion von Korund Komponenten mittels SLE

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades einer Doktorin der Ingenieurwissenschaften genehmigte Dissertation vorgelegt von

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List of Abbreviations

\(\alpha\) Contortion error

\(\alpha - Al_2O_3\) Crystalline sapphire

\(\Delta E\) Energy band gap

\(\Delta n\) Refractive index change

\(\Delta n_b\) Birefringence

\(\Delta x\) Spacial off-set along x-axis

\(\Delta y\) Off-set in y-direction caused by contortion error

\(\Delta z\) Spacial off-set along z-axis

\(\gamma - Al_2O_3\) Amorphous sapphire

\(\lambda\) Wavelength

\(\omega_{\text{laser}}\) Frequency of the laser radiation

\(\Phi\) Angle of incidence

\(\Phi_L\) Phase of light

\(\tau\) Pulse duration

\(\theta\) Half deflection angle

\(\Phi_B\) Diameter of the (laser) beam

\(\Phi_L\) Diameter of the lenses

\(\Phi_s\) Scan field diameter

\(\Phi_{\text{inner}}\) Inner diameter of a tube

\(\Phi_{\text{outer}}\) Outer diameter of a tube

\(A\) Entrance pupil diameter

\(A'\) Maximum laser beam diameter
List of Abbreviations

Al  Aluminum
b  Beam displacement
BFL  Back focal length
BWD  Back working distance
c  Concentration
d  Irradiation depth inside the sample
d_s  Sample thickness
dz  Cross section length of the microchannel
e  Electron charge
E_p  Pulse energy
E_{pL}  Pulse energy at the laser exit
E_{th}  Threshold energy for optical breakdown
F  Effective focal length of a lens
f  Repetition rate
FWD  Front working distance
I  Intensity
L  Entrance pupil position
M^2  The ratio of the BPP of an actual beam to that of an ideal Gaussian beam at the same wavelength
m_e  Reduced electron mass
n  Refractive index
n_a  Refractive index of amorphous sapphire
n_c  Refractive index of crystalline sapphire
n_v  Refractive index in a void
n_{air}  Refractive index in air
n_{ca}  Refractive index of crystalline sapphire which is affected by a stress field
n_{cri}  Critical electron density for optical breakdown
x
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<td>O</td>
<td>Oxygen</td>
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<tr>
<td>$P_{av}$</td>
<td>Average power</td>
</tr>
<tr>
<td>$P_{cr}$</td>
<td>Critical power for self-focusing</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Average surface roughness</td>
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<tr>
<td>$R_{max}$</td>
<td>Maximum surface roughness</td>
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<tr>
<td>$S_a$</td>
<td>Roughness average</td>
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<td>$S_q$</td>
<td>RMS roughness</td>
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<td>$T$</td>
<td>Irradiation time</td>
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<td>$t$</td>
<td>Etching duration</td>
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<td>$T^*$</td>
<td>Temperature</td>
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<td>$T_{layer}$</td>
<td>Average irradiation time of a layer</td>
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<td>$T_{total}$</td>
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<td>$v$</td>
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<td>$Y$</td>
<td>Young’s modulus</td>
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<td>$y$</td>
<td>Length of the microchannel</td>
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<tr>
<td>$z$</td>
<td>Cross section length of the microchannel</td>
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<td>$z_R$</td>
<td>Rayleigh length</td>
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<td>$Z_{Exp}$</td>
<td>Position of the exit pupil</td>
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<td>$2\omega_0$</td>
<td>Focus diameter</td>
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<td>Number of passes</td>
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<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>AOM</td>
<td>Acousto Optic Modulator</td>
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<tr>
<td>BPP</td>
<td>Beam parameter product</td>
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<td>corr</td>
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List of Abbreviations

EDX  Energy Dispersion X-ray spectroscopy

FWHM  Full width half maximum

HF-acid  Hydrofluoric acid

LED  Light emitting diode

N  Number of microchannels

NA  Numerical aperture

NLS  Nano-stereolithography

OM  Optical microscopy

POM  Polarization optical microscopy

RP  Rapid prototyping

RS  Raman spectroscopy

SA  Spherical aberration

SEM  Scanning electron microscopy

SLE  Selective Laser Etching
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Abstract

In dieser Arbeit wird die digitale photonische Produktion von Korund Komponenten mittels eines selektiven laserbasierten Ätzprozesses (SLE) untersucht. Hierzu wird zunächst die Erzeugung von 2D Korund Komponenten mittels ultrakurz gepulster Laserstrahlung und nachfolgendem Ätzen grundlegend untersucht und optimiert. Basierend auf diesen Erkenntnissen wird die Übertragbarkeit des Prozesses für die photonische Produktion von 2 1/2D und 3D Komponenten gezeigt.


In this work the digital photonic production of corundum components by a selective laser induced etching process (SLE) is investigated. Initially, the generation of 2D corundum components using ultra short pulsed laser radiation and adjacent etching is investigated and optimized. Based on the generated knowledge the transfer of the process for the generation of 2 1/2D and 3D components is shown.

In addition, a precision scanner with large numerical aperture (µScanner) is developed. The µScanner’s development leads to a decrease in irradiation time during the photonic production of corundum components. The development of the µScanner enables faster and flexible laser irradiation of customized components, driving prototype development and promoting affordable small series production. The generation of 2 1/2D components in sapphire and ruby is demonstrated with the µScanner.
Chapter 1.

Introduction

Corundum, in the form of sapphire and ruby, was the first precious stone to be used beyond jewelry. In 1704, the unique physical properties of sapphire and ruby, e.g. high hardness, durability, low static and consistent dynamic friction, were firstly understood and used as jewel bearings in watches by Nicolas Fatio de Duillier and Peter and Jacob Debaufre [1]. Sapphire surfaces, with Mohs hardness of 9 and Knoop hardness of 2000, are very hard and durable. A smooth surface is maintained over decades of use, thus reducing friction variability [1]. The invention of jewel bearings made watches more reliable and precise, but also expensive since natural jewels, such as diamond, sapphire, ruby, and garnet were used. In 1902, the production of jewel bearings became more affordable with Auguste Verneuil’s invention of a process for the fabrication of synthetic sapphire and ruby. Since, synthetic sapphire jewel bearings were introduced to many other applications which require friction control and durability. Today, corundum components are found in watches, flow meters, checker valves and as water jet cutting and sandblasting nozzles [2, 3, 4]. Due to its biocompatibility, chemical inertness and durability, corundum is also a desired material in medical applications such as blades, endoscope tips and blood pumps [5].

Historically, jewel bearings were fabricated by hand-grinding the sapphire/ruby using diamond abrasives and different tools for each step/geometry. Early 20th century industrialization, lapping and polishing machines were introduced, enabling larger lot sizes and eventually, mass production.

Watch stone processing is still not as efficient and flexible as it could be. Still today, one watch stone, depending on its complexity, can require up to 40 processing and controlling/inspection steps [6]. The shaping, from the raw material (ruby boule) to the finished product, can take up to 64 days for batches of up to 300 stones [7]. During this process, about 80 - 90% of the raw material is lost [8], making the process very inefficient and time-consuming. In addition, processing tools suffering significant wear due to the hardness of sapphire, thus increasing maintenance and tool cost.

All these attributes qualify manufacturing of jewel bearings as a conventional subtractive manufacturing process which follows the cost curve (fig. 1.1) of traditional economies of scale [9], where unit cost decreases with increasing lot size. The relationship between unit cost and lot size is determined by fixed costs, such as initial investments, which spread over the whole lot's units. Smaller lot sizes have a higher percentage of initial investment per unit and therefore higher unit costs. For conventional subtractive manufacturing, unit costs also scale with product shape complexity and variability. Increasing complexity increases process steps and machinery, resulting in an increased unit cost.

In this thesis, the high material loss, the lack of product flexibility and complexity of con-
Conventional subtractive manufacturing are overcome by using a digital photonic production (DPP) process. DPP in general describes processes where the final component is directly generated from a powder/liquid/solid base and digital data. DPP utilizes photons, often laser radiation, as a wear-less and fast tool. Experts also refer to laser radiation as a tool that "works" as quickly as computers "think" [10].

DPP enables a new way of product and production design determined by product functionality rather than manufacturing restrictions. In addition, a single tool (photons) is sufficient for manufacturing different or more complex components. Therefore, the complexity of a product is no longer dependent of the amount of machines/process steps resulting in a flat cost curve. Moreover, unit cost for a small lot size equals the unit cost for a large lot size since no tool change is required (fig.1.1).

In this work, a subtractive DPP process, Selective Laser Etching (SLE) is used. SLE is investigated and validated as a manufacturing process for gear stones. It is developed into a manufacturing process not only competitive to conventional subtractive manufacturing of gear stones but also more flexible and material/time efficient. In SLE, tightly focused femtosecond laser radiation is utilized to modify the corundum. The focus size and the removed material are in the µm - range. This aids the reduction of the material losses from 90% to 10-20%, depending on the final shape and the tightest sample filling. To reduced the manufacturing time from 64 days to 2-4 days, scanner technology is implemented and irradiation strategies are developed and automated. These improvements together with the cost reduction of laser sources, directly translate into unit cost reduction (fig. 1.1).
Chapter 2.
Objective and Proceeding

The objective of this work is the development of a laser-based fabrication process on the basis of SLE for corundum components that follows the cost curve of DPP. SLE can be considered a DPP process, since a technical drawing is directly irradiated in the material layer by layer. Afterwards, the irradiated areas are removed in an acid bath and the 3D component remains. This process has the potential to be used for the fabrication of complex geometries with minimal material losses and no tool wear. To achieve this objective, the following research questions must be answered:

- What is the correlation between the process parameter, e.g. irradiation speed, numerical aperture, pulse energy, etching time/concentration and resulting microchannel/3D component?
- Does SLE work with low (NA < 0.8) numerical aperture?
- Is it possible to manufacture 3D components with SLE?
- Is SLE possible in ruby?
- How does the resulting 3D component compare to a conventional manufactured watch stone in terms of surface quality?

SLE is a two-step process consisting of an irradiation and etching step. To achieve a reduction of the manufacturing time from 64 days/300 pieces (approx. 5 hours/piece) to 2-4 days/300 pieces, both steps have to be optimized. To minimize the irradiation time $T$, irradiation strategies have to be improved and scanner technology ($\mu$Scanner) has to be implemented. In figure 2.1, the predicted irradiation times $T^1$ of two scanning technologies, an off the shelf 3-axis translation stage used in proof of principle$^2$ and the $\mu$Scanner adapted for SLE as part of this work, are compared.

In section 3, the materials used in this work, sapphire and ruby, are introduced (fig. 2.2). In section 4, the potential of SLE used with these materials and the advantages compared to conventional subtractive manufacturing or lithography are discussed. In section 5, the fundamentals, laser material interaction and selective etching, are discussed. In section 6, the experimental analysis methodology used throughout the project is introduced.

The process development (section 8) is divided in three main sections with the aim to

---

$^1$The irradiation times are predicted based on the maximum possible irradiation speed $v_{\text{max}}$.

$^2$The first microfluidic channels inside sapphire were fabricated by tightly focussing (NA = 0.8) femtosecond laser radiation inside a sample which was moved with a three axis translation stage in order to irradiate lines. The used translation stage allowed a maximum irradiation speed of $v_{\text{max}} = 2$ mm/s, which results in an irradiation time of $T = 5$ s for a 10 mm long microchannel [11].
Figure 2.1.: Predicted irradiation times $T$ for SLE in dependency of the used equipment (dashed line = translation stage, solid line = $\mu$Scanner) and the complexity of the product.

determine a process window for the irradiation of 2D, 2½D and 3D geometries. Accordingly, is the supporting system engineering (section 7) structured (fig. 2.2).

Figure 2.2.: Proceeding. OM: Optical microscopy, POM: Polarization optical microscopy, SEM: Scanning electron microscopy, EDX: Energy dispersion X-ray spectroscopy, RS: Raman spectroscopy, AFM: Atomic force microscopy.

Based on the preliminary trials of SLE of sapphire (proof of principle) [11, 12], which demonstrated the eligibility of SLE for the formation of in-volume microfluidic channels,
the process window for the generation of 2D geometries is determined (section 8.1). For this purpose the dimensions of microchannels (2D) generated with different irradiation parameters, like pulse energy $E_p$, scanning speeds $v$ and repetition rate $f$, are investigated (section 8.1.1). The shape of the microchannel cross section is investigated to define the influence of spherical aberration for different numerical apertures (mainly NA = 0.4, 0.6) in different irradiation depth (section 5.1). Also, the etching parameters, etching duration $t$ and concentration $c$ are investigated for the optimization of the etching process (section 8.1.3). To increase the fundamental understanding of SLE with high repetition rate ($f = 500$ kHz) femtosecond lasers and low numerical aperture focussing (NA $\leq$ 0.6), the structural change of sapphire is investigated using EDX and Raman spectroscopy (section 8.1.4). SEM images of microchannel cross section cuts are used to detect defects, mainly cracks and nano structures, which limit the process window (section 8.1.5). The equipment, used for the investigation of the process window for 2D geometries, consists of a femtosecond laser system, a translation stage and different microscope objectives (section 7.1).

The acquired process knowledge is used in section 8.2 to develop irradiation strategies for 3D components with 2½D geometry\(^3\), such as cylinders and cubes. Therefore, a layer by layer irradiation approach is implemented and the found process parameters are used to optimize the distance between the single irradiated microchannels. The feasibility of SLE for the fabrication of 3D components in 2½D geometry is demonstrated in sapphire and for the first time in ruby.

First experiments for the generation of 3D devices in 3D geometry\(^4\), such as cones or freeform geometries, are conducted (section 8.3) to demonstrate the functionality of the $\mu$Scanner. The investigation of the parameter window for 3D geometries is not conducted in this work and requires further investigations.

The aim of this work is to provide a foundation for the digital photonic production of corundum components by SLE with the acquired process knowledge and the newly developed irradiation system.

\(^3\)The term 2½D geometry is used in this work to describe every geometry which is generated by combining a series of identical 2D geometries

\(^4\)The term 3D geometry is used in this work to describe every geometry which is generated by combining a series of different 2D geometries
Chapter 3.

Materials Used

In this work corundum is used to demonstrate the feasibility of SLE even for hard and brittle transparent materials. The ability to precisely deposit huge intensities (approx. $10^{15}$ W/cm²) inside the crystalline lattice to modify the material but not induce cracking and weakening the surrounding crystalline structure is essential for the SLE process. Corundum, in form of sapphire, is used for initial experiments. In the fine mechanical industry or horology industry, ruby is the preferred material since the red color allows better detection and therefore handling of small components (mm-range). To address these industries the feasibility of SLE for ruby is also investigated and demonstrated.

3.1. Chemical Composition of Sapphire

The main sapphire components are Aluminum $\text{Al}$ and Oxygen $\text{O}$ which form a crystalline structure in the material. In a crystalline structure as well as in amorphous form, the atoms or molecules are arranged homogeneously. Different than in amorphous materials, in a crystalline structure, the arrangement of the atoms is periodically repeated in a three dimensional lattice – the so called space lattice. The smallest cell of the crystalline structure is called elementary cell and is defined by three vectors $a$, $b$ and $c$, the so called basic vectors, and three angles $\alpha$, $\beta$ and $\gamma$ in-between the vectors. By translation along the space lattice, an elementary cell can be superimposed with another elementary cell. This results in a long-range order not found in amorphous materials. The most symmetric crystalline structure of the 14 Bravais lattices (see A.6) is the cubic structure since it has the same lattice parameters in every direction. A structure with identical distances and angles between the single atoms/molecules in every spacial direction also has identical physical properties for each spacial direction and is called isotropic. Most of the crystalline structures have different lattice parameters resulting in different physical properties depending on the spacial direction. They are an-isotopic.

A homogeneous crystalline structure as described above is called single-crystalline. A structure with more than one crystalline orientation is a poly-crystalline structure. The boundary between the crystallites is called grain boundary. [13, 14]

Synthetic sapphire can be produced by different growth methods, either from the gaseous phase, from a solution, from melt or in the solid phase. The synthetic sapphire used in this work is grown by the Verneuil method (grown from melt), where a finely powdered substance (alumina) is melted using an oxyhydrogen flame and afterwards crystallized into a boule (single crystal).

Sapphire is a crystalline dielectric with a large band gap between valence and conduction...
band ($\Delta E_{Al_2O_3} = 10 \text{ eV}$ [15]). Without an external energy supply, no free carriers in the form of electrons are available in sapphire. Due to external excitation by laser radiation, the band gap can be overcome and free electrons can be created (see section 5.3). The difficulty in processing sapphire with laser radiation, is the huge amount of energy required to promote an electron from the valence to the conduction band without inducing large amounts of heat. The laser intensities required for a band gap of $\Delta E_{Al_2O_3} = 10 \text{ eV}$ can be provided by focused femtosecond laser radiation. Due to the uncoupling of the electron and lattice system in the fs-regime, heat is induced into the crystalline structure in a more controlled manner and does not necessarily lead to crack formation.

3.2. Crystal Indexing

For a consistent notation of the different crystal planes, the Miller index ($h'k'l'$) is used. The smallest integer reciprocal ratio of the intersection of the crystal plane and the coordinate axis is described by this index. In the hexagonal lattice structure, a four axis coordination system is often preferred, the Miller-Bravais-system. The system is based on four translation vectors $a_1, a_2, a_3, c$ and is indexed by $(hkil)$[13]. The vector $a_3$ is redundant since a 3D lattice is over-determined with four vectors. To avoid different notations for the same planes an additional condition is necessary

$$i = -(h + k)$$  \hspace{1cm} (3.1)

To convert from the Miller notation to the Miller-Bravais notation the following term applies for planes

$$(h'k'l') \Leftrightarrow (hk[-(h + k)]l)$$  \hspace{1cm} (3.2)
To convert a direction \((u', v', w')\) from Miller to Miller-Bravais notation \((u, v, t, w)\) the following terms are applied

\[
\begin{align*}
  u &= \frac{1}{\sqrt{3}}(2u' - v') \\
  v &= \frac{1}{\sqrt{3}}(2v' - u') \\
  t &= -(u + v) \\
  w &= w'
\end{align*}
\]

(3.3) (3.4) (3.5) (3.6)

In this work, mainly the Miller-Bravais \([13]\) notation is used, with the exception of some references and drawings.

### 3.3. Properties

#### 3.3.1. Sapphire

Sapphire \((\alpha-Al_2O_3)\) crystallizes in the trigonal crystal system with a hexagonal-rhombohedral lattice structure. The symmetry operations of sapphire in the trigonal crystal system are defined in the ditrigonal-scalenoahedral class. The lattice parameters of sapphire are \(a_{1,2,3} = 4.75 \text{ Å}\) and \(c = 12.98 \text{ Å}\) \([17]\). The crystalline lattice is formed by \(Al^{3+}\) and \(O^{2-}\) ions. The \(O^{2-}\) anions are arranged in the closest hexagonal packing with an AB-layered stack. The \(Al^{3+}\) cations are located in the octahedral gaps between the \(O^{2-}\) ions (fig. 3.2), filling two thirds of the octahedral gaps \([18]\). Due to the uneven filling, the \(Al^{3+}\) ions slightly

![Figure 3.2.: Schematic of the arrangement of \(Al^{3+}\) (black circles) and octahedral gaps (small light circles) between two layers of \(O^{2-}\) (large light circle) in the C-plane. \(a_1, a_2\) and \(a_3\) are translation vectors with the length \(a\).[5]](image)

distort the lattice but do not fall outside the stability limits of the octahedron position. In sapphire, instead of replicating every two layers, ABAB, like in an ideal closest hexagonal packing, it takes six layers for the structure to completely replicate itself. The \(Al^{3+}\) ions are arranged between the \(O^{2-}\)-layer according to abc-periodicity. The layer order of \(O^{2-}\) and \(Al^{3+}\) ions is \(AaBbAcBbAbC\) (fig. 3.3).
Figure 3.3.: Schematic of the arrangement of Al\textsuperscript{3+} ions in the octagonal gaps formed by the \(O^2\textsuperscript{-}\) ions in a close hexagonal packing with the layer stacking AB.\[5\]

Due to the hexagonal crystalline structure, sapphire is anisotropic in all optical and physical properties (see table 3.1). Sapphire is birefringent for all directions except along the c-axis. Therefore, knowing the crystallographic orientation towards the optical axis (c-axis) is important for optical and mechanical components and laser irradiation. The orientations of common cuts (c-plane, a-plane) for flat sapphire samples are shown in figure 3.1. Sapphire samples used in this work are all cut in c-plane and all irradiation parameters are optimized for this plane. The laser radiation is focussed parallel to the direction of the c-axis to avoid birefringence affects. Higher thermal expansion \(\alpha = 6.6 \cdot 10^{-6}\) \(^1/\text{k}\) along the c-axis indicates a preferred crack formation along the c-axis may support the SLE process.

Sapphire is transparent for wavelength \(\lambda = 0.18 \ \mu\text{m} - 5.5 \ \mu\text{m}\) and is suitable for optical components such as lenses and infrared windows. The material is suitable for in-volume diffractive gratings or micro devices using femtosecond laser radiation in the near infrared (see Section 8.2).

For mechanical applications sapphire is used because of its high hardness (9 Mohs) at relatively low cost\(^2\). The hardness of sapphire parallel to the c-axis (Knoop 2200 \(\text{kg/mm}^2\)) is higher than perpendicular to the c-axis (Knoop 1900 \(\text{kg/mm}^2\)) \[5\]. Further physical properties of sapphire are listed in table 3.1:

\(^1\)See appendix A.7 for more details of the optical properties.
\(^2\)For example a 1" sapphire watch cover glass costs from 10 - 12 \$ \[1\]
3.3. Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point $T_m$</td>
<td>2,323 K [5]</td>
</tr>
<tr>
<td>Softening point $T_s$</td>
<td>2070 K [19]</td>
</tr>
<tr>
<td>Brittle-to-ductile transition point $T_c$</td>
<td>1025-1090 K [20]</td>
</tr>
<tr>
<td>Thermal expansion $\alpha$</td>
<td>$6.6 \cdot 10^{-6} \text{ K}^{-1} [5]^{1}$</td>
</tr>
<tr>
<td></td>
<td>$5.0 \cdot 10^{-6} \text{ K}^{-1} [5]^{1}$</td>
</tr>
<tr>
<td>Thermal conductivity $\kappa$</td>
<td>$32.3 \text{ W/(m K)} [5]^{3}$</td>
</tr>
<tr>
<td>Density $\rho$</td>
<td>$3.97-3.99 \text{ g/cm}^3 [5]$</td>
</tr>
<tr>
<td>Hardness $^4$</td>
<td>$1525-1800 \text{ kg/mm}^2 [5]$</td>
</tr>
<tr>
<td>Friction coefficient $f$</td>
<td>$^{(c\text{-plane-c\text{-plane})}}0.02 [5]$</td>
</tr>
<tr>
<td></td>
<td>$^{\text{sapphire-steel}}0.22/0.14 [5]^{6}$</td>
</tr>
<tr>
<td>Young's modulus $Y$</td>
<td>$435 \text{ GPa [5]^{7}}$</td>
</tr>
<tr>
<td>Refractive index $n_o$</td>
<td>$^{\parallel c\text{-axis}}1.760 [19]^{8}$</td>
</tr>
<tr>
<td></td>
<td>$^{\perp c\text{-axis}}1.769 [19]^{8}$</td>
</tr>
</tbody>
</table>

$^1$ at $T = 293-323 \text{ K}$
$^2$ at $T = 1,273 \text{ K}$
$^3$ at $T = 298 \text{ K}$
$^4$ Knoop Hardness see A.8
$^5$ Friction coefficient measured over time with a velocity of 0.05 m/s and a force of 1000 N.
$^6$ no lubrication/lubrication, at a pressure of 3.7 GPa
$^7$ at $T = 323 \text{ K}$
$^8$ at $\lambda = 0.5893 \mu\text{m}$

Table 3.1.: Properties of sapphire [5, 19, 20]

3.3.2. Ruby

Corundum can be found in a wide diversity of colors due to small amounts of additives in the Al$^{3+}$ and O$^{2-}$ matrix. If 0.5 – 2 % of the Al$^{3+}$ ions are replaced by Cr$^{3+}$ ions, corundum is red and is named ruby. Each Cr$^{3+}$ ion is surrounded octahedrally by six O$^{2-}$ ions. Like sapphire, ruby has a hexagonal crystalline structure with the lattice parameters $a = 4.76 \text{Å}$ and $c = 12.99 \text{Å} [21]$.

The force of the crystal field created by the oxygen ions around the chromium leads to a separation of energy levels since Cr$^{3+}$ has (different to Al$^{3+}$) a partially filled shell (3 electrons in the 3d shell) [22]. In ruby, electrons can be exited from the ground state $E_1$ to a higher state by absorbing relatively small amounts of energy. The energy of level $E_2$, $E_3$ and $E_4$ are respectively 1.79 eV, 2.23 eV and 3 eV. Energy level $E_2$ is due to selection rules not available to the electrons from the ground state ($E_1$). By absorbing yellow-green ($\lambda = 556.1 \text{ nm}$) and violet ($\lambda = 413.3 \text{ nm}$) light electrons can be exited to $E_3$ and $E_4$. When white light enters a ruby, yellow-green and violet light will be absorbed by the unpaired
electrons. These electrons are excited to higher energy levels. The residual, unabsorbed colors determine the red color of the ruby.

Ruby’s distinct energy levels with one meta stable level $E_2^3$, and its possibility to pump

![Diagram of energy levels in ruby]

**Figure 3.4.** Schematic of Cr$^{3+}$-ions’ energy levels in ruby. Wavelength of the light absorbed or emitted is indicated by the color of the error. Modified from [23]

the material with white light was used in 1960 by Maiman to build the first laser [24]. Ruby lasers were also the first lasers used in the horology industry to drill jewel bearings [25]. With the exception of the special energy level structure, compared to sapphire, ruby has very similar properties (table 3.2).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point $T_m$</td>
<td>2050°C [21]</td>
</tr>
<tr>
<td>Thermal expansion $\alpha$</td>
<td></td>
</tr>
<tr>
<td>$\perp$ c-axis</td>
<td>6.65 $\times$ 10$^{-6}$ K [21]</td>
</tr>
<tr>
<td>$\parallel$ c-axis</td>
<td>7.15 $\times$ 10$^{-6}$ K [21]</td>
</tr>
<tr>
<td>Thermal conductivity $\kappa$</td>
<td></td>
</tr>
<tr>
<td>$\parallel$ c-axis</td>
<td>46.2 W/(m K) [26] $^1$</td>
</tr>
<tr>
<td>$\perp$ c-axis</td>
<td>25.1 W/(m K) [26] $^2$</td>
</tr>
<tr>
<td></td>
<td>12.55 W/(m K) [26] $^3$</td>
</tr>
<tr>
<td>Density $\rho$</td>
<td>3.98 g/cm$^3$ [26]</td>
</tr>
<tr>
<td>Hardness</td>
<td>9 [26], [21]</td>
</tr>
<tr>
<td>Young’s modulus $Y$</td>
<td></td>
</tr>
<tr>
<td>$\parallel$ c-axis</td>
<td>425 GPa [26] $^4$</td>
</tr>
<tr>
<td>Friction coefficient $f$</td>
<td>rubber-steel</td>
</tr>
<tr>
<td></td>
<td>0.25/0.12 [5] $^5$</td>
</tr>
<tr>
<td>Refractive index $n_o$</td>
<td></td>
</tr>
<tr>
<td>$\parallel$ c-axis</td>
<td>1.7638 [26] $^6$</td>
</tr>
<tr>
<td>Refractive index $n_e$</td>
<td></td>
</tr>
<tr>
<td>$\parallel$ c-axis</td>
<td>1.7556 [26] $^5$</td>
</tr>
</tbody>
</table>

$^1$ at $T = 273$ K  
$^2$ at $T = 373$ K  
$^3$ at $T = 673$ K  
$^4$ at $T = 323$ K  
$^5$ no lubrication/lubrication, at a pressure of 3.7 GPa  
$^6$ at $\lambda = 700$ nm

**Table 3.2.** Properties of ruby [5, 21, 26], compare table 3.1 for sapphire.

---

$^3$ Due to selection rules, the excited electrons are not allowed to fall back to their ground states ($E_1$). They must first fall back to a meta stable energy level $E_2$ (1.79 eV). When the electrons in $E_2$ fall back to their ground state, red ($\lambda = 694.3$ nm) light is emitted.
Chapter 4.

State of the Art

4.1. Conventional Machining

Processing of transparent materials, such as sapphire, is currently done with abrasive machining, controlled cracking and breaking or by laser-assisted machining processes. 3D micro devices, like jewel stones for the horologic industry, fine mechanics industry, or nozzles for water jet cutting are manufactured using commercial abrasive processes like grinding, honing, lapping and polishing. Abrasive powders make in general harder then the material they are to process. The powder is moved with a tool over the material to be processed while applying pressure. Therefore, not only the material, but the tool also erodes during machining. For specific shapes, special tools, or a combination of different chipping processes, are required. The chipping processes are mainly categorized by their ability to remove a certain thickness in a specified window of time. In general, the harder the processed material the longer the processing time.

Special tool requirements, high tool wear and the long processing time for hard materials like sapphire and ruby make abrasive machining inefficient. Moreover the material consumed by abrasive machining processes is extremely high since the remaining part’s whole surrounding material is removed. To demonstrate this in numbers, here is an example from the horology industry, where jewel stones are used as gear stones to reduce friction [1].

For jewel stones for mechanical wrist watches up to 30 to 40 machining and inspection

![Image](image.jpg)

Figure 4.1.: Cut ruby crystal grown with Verneuil process sawed into slices (thickness of slices 0.3 – 2 mm) (left) [27]. Different geometries of jewel stones for mechanical watches and watch stone (diameter 0.6 – 1.3 mm)(right) [28].

steps are required to transform the ruby crystal (fig. 4.1 left) into the final product (fig.
4.1 right) [6]. The material losses during the machining processes can sum up to 90% of the raw material\(^1\) [8]. The whole machining process can take up to 65 days [7]. The costs per piece is reduced by fabricating large lot sizes\(^2\). Processing large numbers of jewel stone in parallel decreases the price per piece but also results in an inflexible machining process. The machining of jewel stones follows the schematic cost curve of conventional subtractive manufacturing (see fig. 1.1). The characteristics of conventional machining processes are compared in table 4.1 with laser-based machining processes.

4.2. Machining with Laser Radiation

Fabricating 3D components with laser radiation technologies follow either a top-down or bottom-up approach (fig. 4.2). The top-down approach describes a subtractive process

![Figure 4.2.: a) Top-down approach and b) Bottom-up approach](image)

where bulk material is processed into a final device by removing material. The bottom-up approach describes an additive process where building blocks, for example molecules or particles, are connected by either cross-linking or melting. The main difference between both approaches is the material efficiency. The bottom-up approach is very resourceful since only the required building blocks is consumed to generate the final shape. In the top-down approach material is removed from the bulk material until the final shape is generated. Therefore the top-down approach is less resourceful.

Lithography is a classic example for fabrication of 3D structures in top-down approach by using a succession of 2D photolithography steps (see section 4.2.1)[30]. This approach is often used in structuring semiconductors with small feature size to obtain functional photonics crystal devices [31, 32]. Throughput is low due to the many repetitions required to process multiple layers.

Direct laser ablation is an other example of the top-down approach. Here sapphire is not removed layer by layer by chemical etching but by direct laser ablation. This method is shortly discussed in section 4.2.2. Ablation has no high throughput and the final devices are restricted to a 2\(1/2\)D shape of limited height.

The bottom-up assembly [30] describes the self-organized sedimentation of dielectric nanospheres into ordered 3D opal structures (lattice). After sintering, the nanospheres

---

\(^1\)The price of a half boule of yellowish sapphire crystal grown with Verneuil process is 15.45 €/100 ct, whereas 1 ct = 0.2 g [29].

\(^2\)The annual production of jewel stones for the horology industry of one company (La Pierette) in 2003 was 18 20 million jewels [28].
serve as a 3D mold for the fabrication of silicon photonic crystals [33, 34]. This approach is suitable for the assembly of large periodic structures and has potentially high throughput. However, it provides a limited choice of 3D periodic structures and therefore will not be discussed further.

3D laser lithography [30] exploits nonlinear absorption induced by intense laser radiation. Intense laser radiation absorption results in either "hard" dielectric breakdown in solid dielectrics or “mild” optically-triggered cross-linking of polymers in organic photoresists [35, 36, 37] and photo-polymerizable liquid resins. The nonlinear processes, e.g. two-photon absorption [38, 39, 40] have come to play a dominant role in 3D nano-fabrication, e.g. in nanostereolithography (see appendix A.1). Stereolithography is used for the fabrication of 3D structures in 3D geometry out of polymers, e.g. PMMA, PMGI, DNQ and SU-8, [35, 41, 42, 37]. Stereolithography is not suitable to process hard materials, e.g. sapphire and ruby, and will therefore not be further discussed.

Hard dielectric breakdown is used to develop the SLE process, described in section 5.5.

![Figure 4.3: Cookie-cutter approach](image)

For SLE, a third approach is used which we will call the cookie-cutter approach (fig. 4.3). Similar to the top-down approach, the process starts with bulk material. However, the used tool, focused femtosecond laser radiation, has total access to the material. This enables the irradiation of 2D shapes, "cookies", in every layer. The final shapes (3D) are generated of stacked irradiated layers. Since the focused laser beam and following etching only affect a small area, sub-μm, the final shapes can be packed close together. While not as efficient as the bottom-up approach, this allows higher material efficiency than the top-down approach.

Since they involve laser radiation and/or etching, direct laser ablation and photolithography are discussed and compared to SLE.

### 4.2.1. Lithography

Photolithography is a process used to mass produce 2D structures in the sub-μm range, such as transistors for computer chips, Micro-Electro-Mechanical-Systems (MEMS) and patterned substrates, including sapphire, in LED manufacturing [43, 44, 45, 46]. In photolithography, a mask and lenses are used to transfer 2D structures onto a photoresist\(^3\). Exposing the photoresist through the photomask (\(\lambda = 436 – 193\) nm, 13.5 nm) [47] changes

\(^3\)Photoresist is a light sensitive chemical which is changed chemically and physically in the irradiated area.
the chemical structure of the photoresist. In a subsequent step, called development, the irradiated area is removed by rinsing the area in a solvent\textsuperscript{4}. The 2D structure is then induced into the substrate by etching either with a liquid chemical agent (wet etching) or with a plasma (dry etching). The uncovered substrate is removed either isotropic, if wet-etched, or anisotropic, if dry-etched [48]. Higher aspect ratios (\(\approx 5\) [48]) are achieved and undercuts are prevented with dry-etching. The etching is normally followed by a cleaning step in which the remaining photoresist is removed (also called strip resist).

The whole process chain for a simple 2D pillar structure fabricated with photolithography consists out of at least 8 single steps (fig. 4.4). For a more detailed explanation see appendix A.2. Depending on the required structure different photomasks are required.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4_4.png}
\caption{Schematic of the different steps of a 2D structure fabricated with photolithography.}
\end{figure}

A photomask set normally consists of 20 or more masks. Each mask in a mask set defines a specific photolithographic step in the fabrication process. Due to the decreasing requested feature size in photolithography the fabrication cost of photomask-sets have increased from U.S.$ 500 \text{ k}$ for the 130 nm technology node\textsuperscript{5} to U.S.$ 1 \text{ million}$ for the 90 nm technology node and to U.S.$ 2 \text{ million}$ for the 65 nm technology node [49]. The price for a mask set for 32 nm technology node in 2008 was estimated at U.S.$ 75 \text{ million}$ [50].

Using photomasks, about 80 4" sapphire wafers are patterned per hour [51]. The high expenses for the mask sets are offset if large numbers of 2D structures are fabricated, which makes photolithography an excellent tool for mass production [52]. For small lot size production or even prototyping this technology is too expensive.

Manufacturing 3D structures with photolithography in sapphire is only possible by multiple patterning and geometries are limited by the top-down approach. Also, the fabrication time increases immensely for 3D structures, which makes the whole process more expensive.

\textsuperscript{4}If the irradiated photoresist is removed during the development one speaks of a positive photoresist.

\textsuperscript{5}Describes the half pitch between two adjacent DRAM (Dynamic Random Access Memory) metal lines.
4.2.2. Direct Laser Ablation

3D sapphire components in 2½D shape can be fabricated by direct laser ablation in a top-down approach. Ultrashort laser radiation in the picosecond/femtosecond range is utilized for this purpose, and tightly focused onto the sample surface. By moving the laser beam over the surface results in ablation. The number of passes is define the ablation depth of the feature. Due to scattering of the laser beam on the walls and on ejected particles, the side walls are tapered (fig. 4.5). The crack-free fabrication of a 250 μm thick gear wheel was demonstrated by using the peak intensities \((10^7 - 10^8 \text{ W/cm}^2)\) of a Nd:YAG laser \((\lambda = 355 \text{ nm})\) [53]. However, later publications mention damage to the rear side while structuring the surface and drilling blind holes [54, 55]. Also, Kim et al. demonstrated the ablation of a 250 μm deep and 100 μm wide groove by using ultrashort femtosecond laser radiation (pulse duration \(\tau = 50 \text{ fs}\), wavelength \(\lambda = 800 \text{ nm}\)) in sapphire. He points out that deeper grooves can only be achieved by increasing the width [56]. Further studies comparing different femtosecond and picosecond laser on machining holes in a 1.2 mm thick sapphire sample reveal significant taper and surface damage [55]. At least for one process, direct laser ablation has been proven to be beneficial. Dicing/stealth dicing/scribing/TLS-dicing \(^6\) of brittle materials, especially sapphire, for the fabrication of photonics devices like LEDs can be either done mechanical or with laser radiation. Different kinds of pulse durations (ns-fs, cw), repetition rates and wavelength (255 nm - 800 nm, 1080nm) have been used for this purpose [57, 58, 59, 60]. Laser-based dicing of LED substrates has, depending on the laser, either a higher through put or increases the light extraction efficiency of the LED. In addition laser dicing is in general less material consuming than mechanical dicing since the kerf width is thinner (approx. 30-50 μm compared to 150-250 μm (thickness of the diamond blade) and therefore the LED dices can be much closer together [57, 59, 60]. However, dicing by direct laser ablation requires the substrate to be covered with a photoresist to prevent the ablated material to settle back down on the LED surface. Also, a cleaning step is required after the dicing to remove the photoresist. Stealth-dicing is a much cleaner process since the laser is focused inside the material and a 50 μm layer of substrate is modified. The final separation is subsequently done by stretching the substrate. The drawback of this method is that at

\(^6\)Device separation of LED components which are deposited by MOCVD or CVD on a sapphire substrate.
least 50% of the substrate thickness has to be modified and the modified areas have much rougher surface [60]. TLS-dicing (thermal-laser-separation) is a two step process where an initially mechanically induced scribe is subsequently heated with laser radiation and then immediately cooled. The large difference in temperature induces high tensile forces in the substrate and results in a very smooth crack. TLS-dicing uses cw-fiber laser source, which makes it the least expensive of the dicing methods.

In all three cases, a top-down approach is utilized, where the material is ablated from top to bottom by using multiple passes. This method has the disadvantage that with increasing depth, the laser beam is partially scattered on the remaining wall and either results in a restriction of the ablation depth or a significant taper. Moreover, the devices which can be fabricated with this process are restricted to $3^{1/2}$D geometries due to the geometrical restrictions of the experimental set up.

### 4.2.3. Comparison

All available technologies to process hard brittle materials like sapphire and ruby are compared in table 4.1. Conventional machining, photolithography and direct laser ablation (including all the subtypes) are manufacturing processes especially developed for one industry or application. Therefore, the processes are designed as cost efficient as possible. The single techniques mostly resulting in mass production with no flexibility for shape or changes in demand. Photolithography and direct laser ablation cannot fabricate 3D devices in 3D geometries. With conventional subtractive machining 3D devices with limited 3D geometries can be produced. However, with increasing geometric complexity the fabrication cost increases since additional equipment is required. Also, for conventional subtractive manufacturing, the material efficiency is lowest and the tool wear is high due to the hardness of corundum.

In table 4.1 the deficits of the different manufacturing processes are listed. From the deficits, the request of a machining process for corundum can be deducted which does not require additional tools, has a minimum feature size smaller than 100 $\mu$m, large aspect ratio, no taper and high material efficiency. The only process which has in general no tool wear is a contact-free process, a laser-based process.

In 2006 the fabrication of microchannels in sapphire was first reported by Juodkazis et al. [12]. Tightly focused femtosecond laser radiation (NA = 1.35) was used to modify the material and, subsequently, remove the modified material by etching. In 2007 Wortmann et al. generated microchannels in sapphire with a NA of 0.8. These microchannels had a diameter in the micrometer range and a length of up to 1 mm, resulting in an aspect ratio of 1000:1 [11]. Juodkazis and Wortmann describe the process as a two-step process (fig. 4.6):

1. Irradiation of the transparent material with tightly focused femtosecond laser radiation.
2. Etching the sample using hydrofluoric acid (HF).

In the laser irradiation step the material is only locally modified (in the focal area), no material is removed. Therefore the process is very precise and interaction of the laser radiation and scattered particles are no concern. The capability of this process to
Figure 4.6.: Schematic process for the fabrication of microchannels: 1. Irradiation of the transparent material. 2. Etching of the irradiated sample in HF-acid. The irradiated areas (modified sapphire (mod)) are selectively faster etched than the surrounding material (single crystalline sapphire (SX)) due to the structural change of the crystalline lattice.

generate 3D geometries is theoretical given since the laser radiation is only absorbed by the transparent material in the focal volume. The fundamental mechanisms will be further discussed in section 5.5. In this work a process called SLE (Selective Laser Etching) will be developed on the bases of the process shown by Juodkazis et al.. The reduction of NA, the increase of irradiation speed and the use of turn key laser systems are some of the research questions which will be addressed to develop a competitive manufacturing process.
### Chapter 4. State of the Art

#### Table 4.1: Unique characteristics of conventional machining, photolithography and direct laser ablation and deficits for the fabrication of 3D devices.

<table>
<thead>
<tr>
<th></th>
<th>Conventional machining</th>
<th>Photo lithography</th>
<th>Direct laser ablation</th>
<th>Deficits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td>metal, non-metal,</td>
<td>metal, non-metal,</td>
<td>corundum, dielectrics</td>
<td>limitations for hard, brittle materials</td>
</tr>
<tr>
<td></td>
<td>ceramic, plastic,</td>
<td>ceramic, plastic,</td>
<td></td>
<td>(corundum)</td>
</tr>
<tr>
<td></td>
<td>corundum</td>
<td>corundum</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Required tools</strong></td>
<td>form-specific</td>
<td>form-specific</td>
<td>protection coating,</td>
<td>tool cost, tool wear</td>
</tr>
<tr>
<td></td>
<td>grinding tools,</td>
<td>(mask set)</td>
<td>scribing tool</td>
<td></td>
</tr>
<tr>
<td></td>
<td>abrasive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Minimum feature size</strong></td>
<td>several 100 µm</td>
<td>32 nm</td>
<td>10 µm [59]</td>
<td>100 µm for 3D</td>
</tr>
<tr>
<td><strong>Aspect ratio</strong></td>
<td>3:1 [61, 62]</td>
<td>5:1 [48]</td>
<td>14:1 (30 ns,</td>
<td>small aspect ratio, taper</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>255 nm) [57],</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5:1 (50 fs,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>800 nm) [56]</td>
<td></td>
</tr>
<tr>
<td><strong>Material efficiency</strong></td>
<td>low (losses up to 80-90% [8])</td>
<td>high</td>
<td>20% losses of conventional dicing [59]</td>
<td>low for 3D</td>
</tr>
<tr>
<td><strong>Production volume/machine</strong></td>
<td>high (several 100 pieces parallel)</td>
<td>80 4&quot;/h [51], 100 – 200/hour [63, 64]</td>
<td>middle (20 mm/s) [59]</td>
<td>no flexibility regarding shape</td>
</tr>
<tr>
<td><strong>Equipment cost</strong></td>
<td>several 10,000 $</td>
<td>27 million € [65]</td>
<td>several 10,000 $</td>
<td>high for 3D since different machines are required</td>
</tr>
<tr>
<td><strong>Fabrication capability</strong></td>
<td>2D, limited 3D</td>
<td>2D, 2½D</td>
<td>2D, 2½D</td>
<td>not flexible (2D + 2½D + 3D)</td>
</tr>
<tr>
<td><strong>Manufacturing type</strong></td>
<td>commercial, batch production</td>
<td>commercial, mass production</td>
<td>commercial mass production</td>
<td>no prototyping, no small series</td>
</tr>
</tbody>
</table>
Chapter 5.

Fundamentals

5.1. Focusing of Laser Radiation

Using ultrashort pulsed laser radiation with a pulse duration of several hundred femtoseconds high intensities are achievable. With an unfocused laser beam (beam diameter $\varnothing_B = 5 \text{ mm}$, pulse duration $\tau = 500 \text{ fs}$, pulse energy $E_p = 1 \mu\text{J}$), intensities in the range of $I \approx 10^6 \text{ W/cm}^2$ are reached. To change the structure of the transparent material in the volume, depending on the material, even larger intensities $10^{13} \text{ W/cm}^2 < I < 10^{14} \text{ W/cm}^2$, are required. To achieve these intensities, the laser radiation is focused with microscope objectives.

Microscope objectives consist of lenses with a total focal length $F$ and are described by the numerical aperture (NA).

$$NA = n \cdot \sin \theta \approx n \cdot \frac{\varnothing_L}{2F}$$  \hspace{1cm} (5.1)

The NA is defined by the refractive index $n$ of the surrounding medium and the half opening angle $\theta$. For small angle, the NA can be also described by the focal length $F$ and the diameter of the lenses $\varnothing_L$ in the microscope objective. Therefore, the NA is reduced if the maximal lens diameter is not completely illuminated. The achievable focus diameter of a laser beam is defined by the beam quality of the laser radiation. The Gaussian intensity distribution is defined as rotationally symmetric radiation around z-direction with a diameter of $2\omega(z)$ at the position $z$. The minimal beam diameter at $z = 0$ is $2\omega_0$ (fig. 5.1). The divergence angle $\theta$ which equals the half opening angle of the beam $\Theta/2$ in radians, is defined in the far field by

$$\theta = \lim_{n \to \infty} \frac{\omega(z)}{z}$$  \hspace{1cm} (5.2)

The beam parameter product (BPP) is defined by

$$BPP = \theta \cdot \omega_0 = M^2 \cdot \frac{\lambda}{\pi}$$  \hspace{1cm} (5.3)

The Gaussian beam is diffraction limited, therefore the beam quality factor $M^2 = 1$. The beam quality factor of a real caustic is given by the ratio of the Gaussian beam $BPP_G$
and the BPP of the real beam, and therefore larger than 1.

\[ M^2 = \frac{\text{BPP}}{\text{BPP}_G} = \frac{\theta \cdot \omega_0}{\theta_G \cdot \omega_{0_G}} = \frac{\theta \cdot \omega_0 \cdot \pi}{\lambda} \]  

(5.4)

The larger the beam quality factor the larger is the minimal achievable beam diameter. The focus diameter \(2\omega_0\) can be calculated by

\[ 2\omega_0 \approx \frac{4\lambda F}{\pi \Theta_L} \cdot M^2 \]  

(5.5)

and depends on the wavelength of the laser and the radius of the laser beam. Along the optical axis, the diameter of the laser beam varies within the Rayleigh length

\[ z_R = \frac{\lambda_0}{\pi NA^2 \cdot n} \]  

(5.6)

between \(\omega = \omega_0\) and \(\omega = \sqrt{2} \omega_0\) (fig. 5.1) and can be assumed as nearly constant for a Gaussian beam. The focal length equals double the Rayleigh length and is often described as depth of sharpness. The focal volume is defined by \(2\omega_0\) and \(z_R\) and has for the used microscope objectives a cylindrical shape. Perpendicular to the optical axis (z-axis), the isophotes have a circular shape and along the optical axis they have an elliptical shape.

The intensity distribution along the optical axis (z-axis) in an isophote with the distance \(r\) to the optical axis is given by the equation

\[ I(r, z) = I(0, 0) \exp \left[ -2 \left( \frac{r^2}{a^2} + \frac{z^2}{b^2} \right) \right] \]  

(5.7)

with \(a\) and \(b\) being the semi-major and semi-minor axis of the ellipse [66]. With a numerical aperture of \(NA = 0.6\) and the above mentioned laser parameter, a peak intensity of about \(I = 1 \times 10^{14} \text{ W/cm}^2\) is achieved. For large pulse intensities in this range, linear optics alone is no longer valid. Additional nonlinear propagation effects, like optical Kerr-effect, self-focusing followed by filamentation and self-phase modulation, have to be considered as well. The temporal effect, e.g. self-phase modulation, is not discussed here since it has no affect on the focus shape [67].
5.1. Focusing of Laser Radiation

For high intensities, like those found in a focused femtosecond laser pulse, the refractive index of the material becomes intensity dependent.

\[ n(I) = n + n_2 I(t, r) \] (5.8)

\( n \) is the refractive index of the medium in the absence of the electric field and \( n_2 \) is its nonlinear refractive index. Since the nonlinear refractive index is positive for most materials \( (n_2 > 0) \), the spatial intensity profile leads to a spatial refractive index profile which acts as a focusing lens [69]. The laser beam is focused to an even smaller spot size than the linear optic would allow. The higher the intensities, the larger the focusing power due to the spatial refractive index profile. This effect is called self-focusing and leads to a continuous increase of the peak power of the laser pulse. At a power above the critical power \( P_{cr} \) [69],

\[ P_{cr} = \frac{3.77 \lambda^2}{8\pi n_0 n_2} \] (5.9)

the catastrophic collapse of the laser beam is predicted [70, 71] which leads to damage of the optical medium. In reality, two different effects limit the process of self-focusing. Due to the beam parameter product (BPP), the divergence is increased with increasing focusing strength. Also, with increasing intensity, more free electrons are created in the material, which reduces the refractive index. Accordingly, a defocusing lens is created which counteracts the impact of the self-focusing. In the case of an equilibrium between defocusing and self-focusing, a filament is formed [69]. Due to a constant intensity and electron density over long range, the filament can extend over many Rayleigh lengths [72], and reach a length in the micro to millimeter range inside a material. Permanent damage in a dielectric material is caused by the generation of a high free electron density at high intensities and is called optical breakdown. This effect benefits from a low threshold for self-focusing. The threshold energy \( E_{th} \) for the optical breakdown in the presence of weak self-focusing [73] is related to the NA of the microscope objective.

\[ E_{th} = \frac{I_{th} \tau \lambda^2}{\pi (NA)^2 + I_{th} \lambda^2 / P_{cr}} \] (5.10)

\( P_{cr} \) is the critical power for self-focusing, \( \tau \) is the pulse duration of the laser pulse, \( \lambda \) is the wavelength of the laser radiation and \( I_{th} \) is the intensity threshold for optical breakdown. Typical values of the threshold energy for sapphire vary depending on the laser parameter between \( E_{th} = 1.1^2 - 1.83 \ \mu J / pulse \) [73, 74].

Self-focusing has to be considered for \( NA < 0.65 \) [73], like those used in this work. For smaller NAs, a higher maximum pulse energy is required to modify the material [76]. The critical power for self-focusing in sapphire \( (n = 1.76, n_2 = 3 \cdot 10^{-20} \ \text{m}^2 / \text{W}) \) [68]) when irradiated with laser radiation \( (\lambda = 1045 \ \text{nm}) \) is calculated to \( P_{cr} = 3.1 \ \text{MW} \). For a pulse duration \( \tau = 500 \ \text{fs} \), this equals a pulse energy of \( E_{cr} = 1.55 \ \mu J \). The maximum pulse

\(^1\)The nonlinear refractive index \( n_2 \) is very small for most materials. For sapphire \( n_2 = 3 \cdot 10^{-20} \ \text{m}^2 / \text{W} \) [68].

\(^2\)\( E_{th} = 1.1 \ \mu J / pulse \) \( (\lambda = 800 \ \text{nm}, \tau = 100 \ \text{fs}, NA = 0.65) \) [74]

\(^3\)\( E_{th} = 1.8 \ \mu J / pulse \) \( (\lambda = 1053 \ \text{nm}, \tau = 800 \ \text{fs}, f = 800 \ \text{fs}) \) [75]
energy, due to limitations of the laser system used in this work, is \( E_p = 1.2 \mu\text{J} \). Therefore, self-focusing is not expected to occur with the parameters used in this work.

### 5.2. Spherical Aberration

When focusing ultrashort pulsed laser radiation inside a transparent dielectric, aberrations also lead to a deformation of the focal spot.

Aberrations are used to describe the beam propagation which differs from beam propagation in geometrical optics. The rules of geometric optics are only valid for paraxial rays. Paraxial rays include a small angle \( \theta \) with the optical axis for which \( \sin \theta \approx \theta \) is valid. For larger angles also larger terms in the Taylor expansion of \( \sin \theta \) are important. The third term in the series expansion is used to describe monochromatic aberrations, which include spherical aberration (SA) [77]. Due to the spherical shape of lenses, marginal rays are focused in a different location than rays close to the chief ray (see appendix A.3). The result is an extended focus along the propagation direction (\( z \)-axis) of the laser beam. Spherical aberration can be compensated for in air by using aspheric lenses.

When a laser beam is focused inside a transparent material, spherical aberration occurs as well since the marginal rays strike the surface under a larger angle than the rays close to the optical axis. Therefore, the marginal rays are refracted under a larger angle than rays close to the optical axis and are focused in a different position on the optical axis. For \( \text{NA} < 0.16 \), the effect of the spherical aberration on the focus diameter is smaller than the diffraction-limited extension of the focal point. For \( \text{NA} > 0.16 \), the focus diameter \( 2\omega_0 \) is increased due to spherical aberration [77]. In the propagation direction of the laser radiation, the focus is extended by the value \( \Delta l \) [78].

\[
\Delta l = \frac{d}{n} \left( \sqrt{\frac{n^2 - \text{NA}^2}{1 - \text{NA}^2}} - n \right)
\]  

(5.12)

The extension of the focus depends mainly from the focus depth in the material \( d \) and the \( \text{NA} \) of the microscope objective. For in-volume micro machining, the effect of the spherical aberration has to be considered for \( \text{NA} > 0.5 \) [73].

In this work, microscope objectives are used with which the spherical aberration in a defined depth can be precompensated. The position of the lenses in the microscope objective is changed by turning a correction collar. Therefore, a compensation for the spherical aberration, created when focusing inside a material, is achieved.

### 5.3. Nonlinear Absorption Mechanism

In this work, the material is processed with femtosecond laser radiation with a pulse duration \( \tau \approx 500 \text{ fs} \). This pulse duration is shorter than the electron phonon coupling
time (several picoseconds) [79]. The result is a temporal separation in interaction between laser radiation and electron system, and electron system and lattice. Therefore, material is locally removed on the surface or modified in the focal volume when irradiated. The temporal decoupling between electrons and lattice decreases the heat affected zone and minimizes the risk of crack formation. Thereby, the material processing with femtosecond laser radiation is is more precise compared to nanosecond or picosecond laser processing [80].

Laser radiation in the visible and infrared range ($\lambda = 0.25 - 3 \mu m$) is not linearly absorbed by dielectric materials like glasses or crystals. The band gap of transparent dielectrics ($\Delta E > 3 \text{ eV}$) is larger than the energy of one photon, no energy can be deposited in the material. The energy of a photon from a laser source with the wavelength $\lambda = 1045 \text{ nm}$ is $E_{\text{photon}} = 1.19 \text{ eV}$, smaller than the band gap of a transparent dielectric. By tightly focusing the laser radiation, intensities of $I > 10^{12} \text{ W/cm}^2$ are achieved and nonlinear absorption takes place. Due to nonlinear absorption processes, energy is deposited even in transparent material, which leads to an optical breakdown [69, 76]. Thereby, the material is modified locally. Free electrons are generated by the promotion of electrons from the valence to the conduction band. The necessary energy to bridge the band gap is either provided by photoionization or impact ionization. Photoionization includes multiphoton absorption and tunnel absorption. For the pulse durations used in this work, both multiphoton and tunnel absorption contribute to the photoionization.

Due to high intensities, the possibility for the simultaneous absorption of multiple photons is given (fig. 5.2). For multiphoton absorption, the possibility to absorb $k$ photons is proportional to the intensity $I^k$ [81]. Electrons promoted by this process from the valence to the conduction band are absorbing more energy as free electrons due to the linear process of inverse Bremsstrahlung. By absorbing single photons, the free electrons are promoted to higher energy levels in the conduction band. The energy of the free electrons is partially transferred to electrons in the valence band by collision and thereby more free electrons are created. This process is called impact ionization (fig. 5.2). Again, free electrons are promoted into higher energy levels by linear absorption of photons and create more free electrons due to impact ionization. These free electrons serve as seed electrons for avalanche ionization [82, 83]. If more free electrons are created than lost by recombination, the process is called avalanche ionization (fig. 5.2). The density of free electrons is rapidly increased and the dielectric reveals a temporal metal-like state.

![Figure 5.2: Schematic of the ionization processes (modified from [66])](image-url)
Chapter 5. Fundamentals

Sapphire has a band gap of $\Delta E \approx 10 \text{ eV}$ [15], therefore a minimum of 9 photons have to be simultaneously absorbed. Accordingly, very high intensities are required. High laser intensities lead to a deformation of the band structure in sapphire. Therefore, tunnel ionization becomes more likely, but multiphoton ionization remains the dominant ionization process. Since it is not the only participating ionization process only 6 photons ($k = 6$) have to be simultaneously absorbed [84]. As reported by different groups for sapphire, intensities in the range of $I \approx 10^{13} \text{ W/cm}^2$ are sufficient to modify sapphire [84, 85].

5.4. Permanent Refractive Index Change

The induced nonlinear absorption processes (see section 5.3) result in an increasing density of free electrons. It is generally accepted [66, 76, 80, 82, 86, 87] that the optical breakdown occurs when the critical electron density $n_{\text{cri}}$

$$n_{\text{cri}} = \frac{m_e \omega_{\text{laser}}^2}{4 \pi e^2}$$  \hspace{1cm} (5.13)

is reached. In this formula, $m_e$ is the reduced electron mass, $\omega_{\text{laser}}$ is the frequency of the incident laser radiation and $e$ is the electron charge [88]. For the majority of transparent dielectrics, the ionization threshold is found at intensities $10^{13} \text{ W/cm}^2 < I < 10^{14} \text{ W/cm}^2$ for laser radiation with the wavelength of $\lambda \sim 1 \mu\text{m}$. The energy of the laser radiation is transferred to the electrons in the conduction band in an intense short pulse (here $\tau = 500 \text{ fs}$) [89]. This is much shorter than the electron-phonon coupling time in sapphire ($t \approx 10 \text{ ps}$) [90].

The thermalization of the free electrons, including electron-electron scattering and electron-phonon scattering, can take from several picoseconds to tens of picoseconds depending on the material [90]. Temperatures in the focal volume up to $T^* = 2000 ^\circ\text{C}$ and more, depending on the laser parameter, are predicted [88, 91, 92] and the material is melted. A high pressure, high temperature region is created which is thermally expanding. The pressure build up is released radially in a shock wave, similar to a micro-explosion [93]. With values of up to 2.7 TPa [88], the pressure exceeds the Young´s modulus of sapphire, $Y = 400 \text{ GPa}$ [88], and many other materials. At a pressure higher than the Young´s modulus, interatomic bonds are destroyed while the shockwave (elasto-plastic wave) propagates from the hot center of the focus volume into the cold surrounding material ($t \approx 0.01 - 800 \text{ ns}$ [90]). In addition, permanent damage, like the formation of a void or cracks, are created by the elasto-plastic wave [90]. With initial thermal diffusion (ns-range), the temperature of the irradiated area is reduced and the material begins to re-solidify. If the cooling time of the molten volume is very short, thermal quenching occurs (phase transition from amorphous to crystalline is no longer possible) and the material solidifies with an amorphous structure. Due to the structural and density changes in the focal volume, stress is induced in the surrounding material as well as strain in the focal volume. Density changes as well as stress result in a local change of the refractive index.

In sapphire, a sharp boundary between shock amorphized sapphire and crystalline sapphire...
phire is found after irradiation with a tightly focussed femtosecond laser [12]. Also, a void is observed in the center of the focus volume. This is explained by a shock wave propagating from the center of the focal volume to the outside, compressing the surrounding material, and a rarefaction wave propagating from the outside to the center, creating the void. The energy, and therefore the pressure, of the shockwave then dissipates. When the pressure equals the Young’s modulus, the shockwave is converted into a sound wave. The sound wave propagates further through the material without leaving any permanent changes [94]. The size of the laser-induced modification in sapphire depends on the laser and focusing parameters. In the focal volume, a reduction in refractive index of up to $\Delta n \approx 1 \cdot 10^{-3}$, caused by the reduced density in the focal volume, was measured [95]. In the area surrounding the focal volume (crystalline sapphire), stress-induced birefringence results in an increased refractive index [96]. Depending on the laser and focusing parameters, the stress-induced birefringence extends several tens of micrometers into the crystal [96]. In single experiments with multi-pulse exposure of the focal volume a change from amorphous to polycrystalline phase was discovered [91, 97]. It is assumed that the repeated heat input has a similar effect on the shock-amorphized sapphire as thermal annealing [91, 98].

5.5. Selective Etching

Selective etching of laser irradiated material was initially used as an investigation tool to enhance the structural changes of a waveguide cross section [99]. In 1998, the first investigations in photosensitive glass using femtosecond laser radiation were conducted by Kondo et al. [100]. The first microchannels irradiated in glass and etched with an aqueous solution of HF were fabricated by Marcinkevicius et al. in 2001 [101]. Later, different groups investigated the irradiation with tightly focused femtosecond laser radiation followed by etching in different transparent materials. The first tests of etching sapphire irradiated with tightly focused femtosecond laser radiation (NA > 1, $\tau \approx 200$ fs) were undertaken by Juodkazis in 2006 [12]. In 2007, it was shown by Wortmann et al. [11] that the fabrication of microchannels in sapphire is also possible when focussing with numerical apertures NA < 1 and using pulse durations of $\tau \approx 500$ fs. Recently, the fabrication of microchannels with ps-laser radiation ($\tau = 10$ ps) and adjacent etching in HF acid was demonstrated [102].

Due to the high intensities of focused femtosecond laser radiation, energy is deposited in the material via nonlinear absorption processes (see section 5.3). In the material, a shockwave is caused by the absorbed energy which leads to a densification of the material and a change in the crystalline structure (amorphization) around the center of the focal area [12, 94]. High resolution transmission electron microscopy (HR-TEM) revealed atomic dislocations in the crystalline structure [97]. In these investigations, a clear boundary is found between monocrystalline and shock-amorphized/polycrystalline sapphire. This boundary is located where the pressure of the shock front becomes equal to the internal pressure of sapphire, the Young modulus $E \approx 400$ GPa (the cold pressure) [97]. The change in the density of sapphire also results in a refractive index change (see section 5.4). In addition, birefringence is induced by the pressure caused by these structural changes. The shock-amorphized region of the sapphire can be wet etched in an aqueous solution of
hydrofluoric acid (HF-acid) or potassium hydroxide (KOH) [12]. The high etching selectivity of up to 1000:1 [11] is not yet completely understood [103]. Possible explanations include physical enhancement of etching due to amorphization, high defect density [104] and even shock-induced chemical modification [105, 106]. Juodkazis et al. point out a decrease of the average Al-O-Al angle due to the compaction in the amorphous area of sapphire. This reduction of the Al-O-Al angle is equivalent to the formation of a more basic (Lewis-base) material that has a higher reactivity to acidic solutions [12].
Chapter 6.

Analysis Methods

During the process development different analysis methods are used to evaluate the parameter variation. The purpose and use of the analysis methods are explained in the following sections.

For some investigations cross section cuts are prepared to inspect the width and length of the microchannels. The cross section cuts are generated by cutting the sample with a diamond wire saw perpendicular to the irradiated tracks. The cross section surface is prepared for the analysis procedure described below by polishing. First, the cross section is smoothed out by removing 10 - 50 µm of the material in a process called lapping. Second, the surface is polished to optical quality ($R_a \approx 1$nm). The machine used for this process is a Logitech PM5-Lapping and Polishing machine. For the lapping step, silicon carbide powder with a grain size of 9 µm is used. The polishing suspension (slurry) SF5 has a grain size of 32 nm.

6.1. Optical Microscopy

Following the etching transmitted-light microscopy is used to measure the length $y$ of the generated microchannel. Since the modified and removed material has a different refractive index than the modified and remaining material, both areas are well distinguishable.

Figure 6.1.: Through light microscope image of etched microchannel. The etched length $y$ and modified sapphire are separated by an etch stop.
Hereafter, the area where the material is removed during etching will be referred to as microchannel. The length $y$ is used as a quantification factor of the etching process with respect to the used irradiation and etching parameters. The error on the channel length measurement is set to be $\sigma_y = \pm 2 \mu m$. To avoid confusion, this systematic error is not shown in the plots.

6.2. Polarization Microscopy

Laser irradiation leads to a change of the crystalline structure, e.g. polycrystalline or amorphous. Without TEM investigation, the status of the crystalline structure can not be clearly specified. Therefore, laser irradiated areas will be categorized as modification. Areas with a modified crystalline structure induce stress spreading out into unirradiated single crystalline areas. Due to the stress, an indirect change is induced into non-irradiated areas which might result in a change of the optical properties of the crystal towards the laser radiation. To further investigate material changes, some samples are investigated with polarization microscopy.

The sample is placed between two crossed polarization filters. The bottom polarizer transmits linear polarized light. If the material in-between the polarizers does not change the lights polarization direction, the 90° turned second polarizer extinguishes light transmitted through the sample. In this case the viewed image is black, which is generally seen for isotropic materials.

Optical anisotropy materials induce birefringence, which means the polarization direc-

![Figure 6.2.: Typical polarization microscope image of a cylinder irradiated in sapphire.](image)

...tion/vector of the light is rotated while passing through the material. This anisotropy either can be caused by the formation of different crystalline orientations (polycrystallinity) in the material or by stress. Stress leads to a direction and location dependent refractive index change $\Delta n$, which results in an anisotropy that changes the phase $\Phi_L$ of the linear polarized light while propagating through the sample.

Sapphire is, because of its hexagonal crystalline structure (see Section (3.3.1)), an anisotropic...
material. Along the c-axis ([0001]) sapphire does not reveal any anisotropies. Therefore, all investigations using polarization microscopy are conducted parallel to the c-axis of sapphire.

When investigating a cylinder irradiated in sapphire with polarization microscopy in the direction of the c-axis, the appearance of the typical isogyre cross (fig. 6.2), a shamrock-like stress field in the exterior of the cylinder. The shape of the stress field is an artifact and is in reality distributed circular around the irradiated cylinder. Disregarding the artifact areas, the dark areas represent stress-free areas and bright areas represent laser-induced stress. For the investigation of all cylinders in one sample, the incident light intensity is kept constant. Therefore, the brighter the areas in the polarization microscope image the larger the induced stress.

### 6.3. Scanning Electron Microscopy

Irradiating sapphire to generate microchannels induces stress in the material which can lead to stress-induced changes of the refractive index or to crack formation. When using optical microscopy both effects can increase the error of the measured dimensions, microchannel cross section length $dz$ and width $w$. Therefore, a scanning electron microscope (SEM) is utilized to measure $dz$ and $w$. SEM images are also used to investigate microstructures e.g. nano planes and cracks.

Using SEM with a ultrahigh vacuum and a special sample holder for charge reduction, the sapphire surface does not require a thin conductive metal layer coating. A gold layer would prevent gathering information from back scattered electrons and by this drastically reduce the material contrast. Thereby, cross sections of the modified but not etched sapphire can be investigated due to a difference in material properties towards the crystalline sapphire. The achievable lateral resolution is in the range of 10 nm. For most of the investigations a table top SEM (Phenom Pro) from Phenom World is used.

### 6.4. Energy Dispersive X-Ray Spectroscopy

A SEM-EDX combi-device from FEI is used for the elemental analysis of the sample in the irradiated as well as in the non-irradiated regions. The area of interest is selected using the SEM, then the X-ray detector measures the emission spectrum of the exited electrons while relaxing to their ground state. Each element has a unique atomic structure and therefor a unique set of peaks in the X-ray spectrum. The detection threshold is limited to elements with a proton number larger than 4.

A possible change in material composition between the irradiated/modified and the not irradiated/crystalline material is investigated with the EDX-measurement.

### 6.5. Raman Spectroscopy

Raman spectroscopy can be used to detected changes in the crystalline structure or in the interatomic bonds by either a shift or disappearance of the Raman peaks. Also stress...
and cracks in the crystal can alter the Raman spectrum. The cross section of the laser modified areas in sapphire is investigated using Raman spectroscopy. Active vibrational modes interact with the monochrome light used in a Raman spectrometer. This interaction (scattering) is measured as a shift in the Raman spectrum (difference between irradiated and detected light). Due to the crystalline structure and symmetries, every crystalline material has a specific Raman spectrum by which it can be defined.

Sapphire ($\alpha - Al_2O_3$) has a rhombohedral crystal structure belonging to the space group $D_{3d}^6$. A primitive unit cell contains two units of $Al_2O_3$ (ten atoms) resulting in 30 $\Gamma$-point vibrational modes which are separated in optical modes $2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u$ and acoustical modes $1A_{2u} + 1E_u$. Seven of these vibrational modes are Raman active ($A_{1g}$ and $E_g$).

For the Raman measurement (inVia Raman Microscope from Renishaw), laser radiation of the wavelength $\lambda = 514$ nm is focused with a microscope objective (50X, NA = 0.75) onto the polished cross section of a laser modification. The laser power of the frequency doubled laser is adjusted to a few mW after the microscope objective to avoid further modification of the area of interest. For the measurement range of $k = 198.92 – 1153.39$ cm$^{-1}$ a spectroscopic grating with 1800 lines/mm is chosen. The irradiation time for each measurement is $t = 1$ s, whereas in total 10 measurements are conducted.

### 6.6. Atomic Force Microscopy

For the process development, surface roughnesses of the final micro component must be close to or better than the surface roughness generated by mechanical grinding (conventional machining).

The surface roughness of single samples, eg. sapphire cylinder and cubes, after etching is measured by using an atomic force microscope (NANOS 806 attached to N8 RADOS) from Bruker Nano. The accuracy of the measurement depends on the geometry of the probe (cantilever tip), if the tip shape is changed, due to damage, the resulting measurement becomes inaccurate. For best results, a cantilever with a diamond tip is used. Diamond (10 Mohs) is slightly harder than sapphire (9 Mohs) and in case of contact will not be damaged immediately.

The measurement is performed in "tapping mode" which is a dynamic contact mode that allows much higher scanning speeds than a contact mode and prevents the sample as well as the probe from being damaged. The free amplitude of cantilever oscillations is carried between 90 and 180 nm. The measurement is undertaken with a scan speed of 0.2 lines per second or $v = 16$ $\mu$m/s. The image resolution is 512 x 512 pixels. The roughness parameters $S_a$ (roughness average) and $S_q$ (RMS roughness) are calculated after 1st order plane correction and 1st order LMS fit.
Chapter 7.

Systems Engineering

System engineering describes the development of the "µScanner". The µScanner is the enabling technical component to develop Selective Laser Etching from fundamental research to a state of the art technology for the digital photonics production of corundum components. The main development motivation are the deficits of other manufacturing technologies. These technologies are unable to provide the flexibility to fabricate 2D and 3D geometries. Moreover, the freedom of shape is a feature that enables small series production and prototyping. This scanner is a major step in the potential mass production of corundum components. Using a nonlinear absorption process, transparent material can be processed on surface but also in-volume. These attributes, combined with an increased irradiation speed and therefore reduced manufacturing times, enable a process to be attractive for industry.

The development of the µScanner is divided in three subsection:

1. Lab set-up
2. Integration of galvanometric scanner
3. Implementation of software components

To prove the principle of SLE, a simple lab set-up is used (see section 7.1). The first experiments are conducted by focusing femtosecond laser radiation tightly into a sapphire sample by using a microscope objective with high numerical aperture. The sample is positioned on a translation stage and moved with the x/y-axis below the laser beam with a maximum speed of \( v = 2 \text{ mm/s} \). In this development stage, all components are controlled manually and individually. This simple set-up is sufficient to irradiate single lines for the investigation of the etching ratio at different processing parameters.

For the irradiation of 2D areas (planes, cuts) in the sample volume, the translation axes are programmed. The first problems occur if the irradiated plane is smaller than the sample. Crack form at the reversal points of the tracks. The damage threshold in this area is exceeded due to lack of controllability of the laser power in relation to the scanning speed. Moreover, due to the low maximum speed \( v = 2 \text{ mm/s} \) of the translation axis, the irradiation time for a plane of 0.15 mm\(^2\) is 11 minutes and 15 seconds\(^1\). In addition, the programming effort for more complex 3D structures is immensely increased.

To improve the irradiation time for 2D geometries, a galvanometric scanner with a maximum scanning speed \( v = 100 \text{ mm/s} \) is implemented. In parallel, the optical paths (laser beam path, imaging beam path and illumination path) are designed and optimized (see

\(^1\text{length } l = 500 \text{ µm}, \text{ width } w = 300 \text{ µm}, \text{ distance between lines } \Delta x = 1 \text{ µm (in the following called off-set)}, v = 2 \text{ mm/s}, \text{ delay when changing direction } \Delta t = 1 \text{ s, focus size } 2\omega_0 = 1 \text{ µm} \)
section 7.2). This improvements allow to irradiate a plane with the size of $0.15 \text{ mm}^2$ with $v = 50 \text{ mm/s}$ now in about 10 seconds instead of 11 minutes and 15 seconds. In addition, the scanner is combined with a modulator, to switch the laser radiation on and off to avoid crack formation at the reversal points. The size of the scan field, and by that the size of the irradiated structure in the work space, is defined by the equipped microscope objective (table 7.3) and ranges between $\varnothing = 0.5 - 1.2 \text{ mm}$. The galvanometric scanner, integrated in a microscope beam path, is called $\mu$Scanner. For focusing and positioning of the sample, the $\mu$Scanner is equipped on the z-axis of the translation stage. Although the $\mu$Scanner and the translation stage are separately controlled, the irradiation of $2^{1/2}$D geometries (e.g. cylinder) is possible with this set-up.

To overcome the limitation of small work spaces, communication software is implemented between scanner and translation stage (see section 7.3). The scanner software controls the translation stage enabling the irradiation of every requested 2D geometry size within the movement range of the translation stage (150 mm x 150 mm). The requested work space is then broken down into tiles, the size of a scan field, and stitched together by moving the sample with the translation axis from one tile to the next.

To achieve the irradiation of 3D geometries, a CAD/CAM software is implemented. Since the combined communication of $\mu$Scanner and translation axis does not allow "on the fly" irradiation\(^2\), 3D geometries are irradiated layer by layer. This is not a disadvantage since the homogeneous irradiation, and by this modification of transparent materials, requires in most cases a bottom to top irradiation.

### 7.1. Equipment

In this work, two different laser systems are used for the experimental investigations of SLE. Both laser systems have quite similar specifications and emit ultrashort pulsed laser radiation in the near infrared spectral range.

1. A Yb-glass fiber chirped pulse amplifier system (µJewel D-1000) from IMRA with a central wavelength of $\lambda = 1045 \text{ nm}$ ($\Delta \lambda = 2 \text{ nm}$), a pulse duration of about $\tau = 500 \text{ fs}$, a maximum average power of $P_{\text{av}} = 1.25 - 1.57 \text{ W}$ and an adjustable repetition rate $f = 100 \text{ kHz} - 5 \text{ MHz}$ is used. The emitted laser radiation is linear polarized with a beam quality of $M^2 = 1.6$. To adjust the pulse duration to the minimum of about $\tau = 500 \text{ fs}$ for each repetition rate the laser system is equipped with an external compressor. The measured laser beam is $\varnothing_B = 5 \text{ mm}$ in diameter after the compressor. The exact parameters for each repetition rate and the characterization of the laser beam are shown in appendix A.4. If required, the laser can be equipped with an accousto-optic modulator (AOM) to switch the laser beam on and off. The implementation of the AOM leads to a distortion of the laser beam profile (see appendix A.4).

2. A fiber chirped pulse amplifier system, Satsuma, from Amplitude Systèmes emits radiation of a central wavelength $\lambda = 1030 \text{ nm}$ ($\Delta \lambda = 5 \text{ nm}$), a pulse duration of $\tau = 480 \text{ fs}$ and an average output power of $P_{\text{av}} = 5 \text{ W}$. Its repetition rate is adjustable $f = 0.1 - 27 \text{ MHz}$. The emitted laser radiation is linearly polarized and almost diffraction limited ($M^2 = 1.2$). The laser is equipped with a built in AOM

\(^2\)Scanner mirror and translation stage axis are operating at the same time.
which does not affect the beam profile (see Appendix A.4). The measured beam diameter is \( \varnothing_B = 2.2 \) mm in diameter at the laser exit. A telescope is used to extend the beam diameter to \( \varnothing_B = 5 \) mm.

The specifications of both laser systems are summarized in table 7.1.

<table>
<thead>
<tr>
<th>Laser</th>
<th>avg. power ( P_{av} ) [W]</th>
<th>wavelength ( \lambda ) [nm]</th>
<th>repetition rate ( f ) [MHz]</th>
<th>pulse duration ( \tau ) [fs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu \text{Jewel} )</td>
<td>1.2 – 1.5</td>
<td>1045±2</td>
<td>0.1 – 5</td>
<td>440 – 580</td>
</tr>
<tr>
<td>Satsuma</td>
<td>5</td>
<td>1030±5</td>
<td>0.1 – 27</td>
<td>480</td>
</tr>
</tbody>
</table>

**Table 7.1.** Specifications of the laser systems.

The laser beam is focussed into the sample using microscope objectives with different numerical apertures (NA). The microscope objectives are equipped with a continuously adjustable correction collar to minimize the focus extension due to spherical aberrations (see section 5.2). All used microscope objectives are polarization maintaining. The size of the entrance/exit pupil varies for different microscope objectives. If the exit pupil is not completely illuminated by the 5 mm laser beam, the NA of the microscope object is reduced NA\(^*\) (see table 7.2). If different microscope objectives are utilized in the same set-up, the parfocal length\(^3\) should ideally be the same. In this way the position of the microscope objective has not to be corrected when switching between different microscope objectives. For microscope objectives from Zeiss and Olympus (newer generation), the parfocal length is 45 mm as depicted fig. 7.1. The position of the exit pupil \( Z_{\text{ExP}} \) never-

![Figure 7.1.](image-url)  
**Figure 7.1.** Schematic of a Zeiss microscope objective with the working distance \( WD \) and the exit pupil position \( Z_{\text{ExP}} \).

\(^3\)The parfocal length is the working distance and the unthreaded length of the microscope objective.
<table>
<thead>
<tr>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>LD Achromat Zeiss</td>
<td>20x</td>
<td>0.45 (0.3)</td>
<td>0 – 1.5</td>
<td>1.66</td>
<td>4.16</td>
<td>-12.6</td>
</tr>
<tr>
<td>LD Achromat Zeiss</td>
<td>40x</td>
<td>0.6 (0.6)</td>
<td>0 – 2</td>
<td>1.11</td>
<td>1.85</td>
<td>-10</td>
</tr>
<tr>
<td>LCPLN20XIR Olympus</td>
<td>20x</td>
<td>0.45 (0.28)</td>
<td>0 – 1.2</td>
<td>1.48</td>
<td>3.29</td>
<td>-3</td>
</tr>
<tr>
<td>LCPLN50XIR Olympus</td>
<td>50x</td>
<td>0.65 (0.65)</td>
<td>0 – 1.2</td>
<td>1.02</td>
<td>1.58</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

Table 7.2.: Specifications of the utilized microscope objectives. The values in brackets are the real numerical apertures at a laser beam diameter of 5 mm.

For the first investigations and the proof of the principle of SLE, a simple set-up is used. This set-up consists of a laser source, a positioning stage, optical elements for beam guiding and a microscope objective (fig. 7.2).

![Figure 7.2. Schematic of the set-up for the irradiation of single lines in the volume of a transparent sample.](image)

The laser beam is guided by silver mirrors from the laser source towards the positioning stage. In the beam path, a $\lambda/2$-plate and a thin-film polarizer are positioned. The thin-film polarizer has an extinction rate of 1000:1. By rotating the $\lambda/2$-plate, the polarization of the laser beam is rotated as well. After the polarizer, the laser beam has the same polarization as before the $\lambda/2$-plate. However, the power of the laser beam is reduced by the fraction of the laser beam that is extinct by the thin-film polarizer. The power of the laser beam is varied continuously by rotating the $\lambda/2$-plate.

With the above-described microscope objectives, the laser beam is focused in the volume of a transparent sample. The sample is mounted with a kinematic three point mount on the x-y-axis of the positioning stage. A CCD-camera, before the microscope objective, is used to ensure a parallel sample adjustment towards the x-y-translation plane of the stage. Depending on the NA of the equipped microscope objective, a tilt of less than 2 mrad
7.2. Adaptation of µScanner

The equipment presented in the last section is suitable for fundamental research and initial investigations. For more complex geometries and for process development the irradiation speed has to be increased. Both laser systems support larger irradiations speeds at large pulse overlap due to adjustable and high repetition rates (kHz - MHz). The implementation of a galvanometric scanner head is the next step in the tool development. Galvanometric scanners are designed for high-speed material processing applications. According to the request from scanner manufactures and industry customers, different lens systems are available for optimal performance and seamless implementation in the scanner system. The largest challenge in this work is that there are no suitable lens systems available to achieve intensities above the threshold for optical breakdown, \( I_{th} \approx 5 \cdot 10^{13} \text{ W/cm}^2 \) in the focal spot, to modify corundum. Commercially available telecentric f-theta objectives are only suitable to focus the laser beam to a spot size of 15 - 20 \( \mu \text{m} \) in diameter. Accordingly, the available microscope objectives have to be implemented with the galvanometric scanner by designing the optical paths. Moreover, for process observation, a camera and suitable illumination is required. The different optical paths (imaging, illumination and laser beam paths) are implemented and combined with the galvanometric scanner.

7.2.1. Galvanometric Scanner

Galvanometer scanners are high performance rotary motors for optical applications. The laser beam is deflected by a mirror which is mounted on the motor section. By rotation, the laser beam is deflected along one axis. 2D patterns are generated by combining two galvanometer scanners. For galvanometer scanners, the load of the mirror (depending on the size of the mirror) is matched to the motor section to ensure high speed and high positioning precision over long lifetime. A scanner unit is equipped with a lens to focus the laser beam on the work piece. Different lens types are favoured for different applications and their requirements. For SLE the process requirements are listed below:

- Threshold intensity for optical breakdown \( I_{th} \)
- Minimum aberrations
- Circular focus geometry
- Constant scan velocity

\( ^4 \)combined use of the µScanner and the positioning stage
Plane irradiation area

The process requirements are discussed in more depth in section 8.1. Using spherical lenses results in a curved focal plane (figure 7.3 a). With flat-field objectives (figure 7.3 b) the beam is scanned over a plane scan-field. The distance x by which the focal spot is moved at a deflection angle $\theta$ is given by

$$x = F \cdot \tan(\theta)$$  \hspace{1cm} (7.1)

with $F$ being the effective focal length of the lens. However, the scan velocity $v_s$ is not constant with respect to the scan angle $\theta$. The scan velocity is accelerated as $\theta$

![Figure 7.3: Lens performance of different focusing objectives for a galvanometric scanner.](image)

A constant scan velocity over the entire scan field is important for many applications. It ensures a constant energy density, due to a constant pulse overlap, over the scanning plane. This deficiency can be overcome by either a special design in the scanner electronics or by using flat-field lenses with built-in negative distortion (barrel), so called f-theta objectives (figure 7.3 c). The focus displacement $x$ from the optical axis is defined by

$$x = F \cdot \theta$$  \hspace{1cm} (7.2)

and is directly proportional to the scan angle $\theta$. Therefore, the scan velocity $v_s$ is constant over the entire scan field. Some f-theta objectives are also telecentric, which refers to the property that every incoming ray, independent of its orientation to the lens surface, strikes the work surface in a normal angle ($\phi = 0$) (figure 7.3 d, 7.4). This attribute ensures that the focus spot has the same size and a circular geometry. Accordingly, the intensity in the focal area is the same for every spot in the scan field. To achieve the same scan field size as with non-telecentric objectives, the diameter of a telecentric f-theta objective is much larger and must be at least as large as the active scan area. The only lens system which is suitable for SLE is the telecentric f-theta objective, provided the intensity threshold $I_{th}$ for optical breakdown is met. To calculate $I_{th}$ the objective parameters are discussed first.

The entrance pupil of the scanner lenses is located in front of the first lens, at a distance $FWD$ from the lens housing. For ideal performance and to avoid vignetting, the rotation point of the laser beam (scanner mirror) should be located at the entrance pupil. If this is not the case, the f-theta performance and the field curvature are compromised. For single-mirror (single-axis) scanner units, this is not an issue, but for two-mirror scanner units, the points of rotation do not coincide. For 2D scanner units, the entrance pupil position
is generally located between the mirrors \( M_1 \) and \( M_2 \), at a distance \( L = d_2 + \frac{1}{2}d_1 \) (fig. 7.4).

\[
\text{Figure 7.4.: Scanning objective parameters [107]: FWD: Front working distance, BFL: Back focal length, BWD: Back working distance, } d_2: \text{ Distance mirror } M_2 \text{ lens housing, } d_1: \text{ Distance mirror } M_1 \text{ mirror } M_2, A: \text{ Entrance pupil diameter, } A': \text{ Laser beam diameter, } \theta: \text{ Half deflection angle, } \Phi: \text{ Angle of incidence.}
\]

The maximum laser beam diameter \( A' \), at a distance \( L > d_2 \) from the entrance pupil with the diameter \( A \), depends on the maximum half deflection angle \( \theta \) and the distance \( L \).

\[
A' = A[1 - (2L/A)\tan(\theta)]
\]  (7.3)

Consequently, minimizing the distance \( L \) results in a larger maximum laser beam diameter \( A' \).

The minimal focus size, \( 2\omega_0 \), which can be achieved with a commercially available f-theta objective with a focal length of \( F = 32.8 \text{ mm} \)\(^5\) at a laser beam diameter of \( \varnothing_B = 5 \text{ mm} \) is calculated using the beam parameter product

\[
\omega_0 = \frac{M^2 \lambda}{\pi \theta}
\]  (7.4)

and the relation between half angle of aperture \( \theta \), beam radius \( \varnothing_B \) and focal length \( F \).

\[
\theta = \arctan\left(\frac{\varnothing_B}{F}\right)
\]  (7.5)

The focus size \( 2\omega_0 = 13.99 \mu m \) of this telecentric f-theta lens results in a laser intensity \( (I = 1.2 \cdot 10^{12} \text{ W/cm}^2 \text{ @ } P_m = 0.6 \text{ W}, f = 500 \text{ kHz}, \tau = 500 \text{ fs}) \) below the threshold for optical breakdown \( I_{th} \approx 5 \cdot 10^{13} \text{ W/cm}^2 \) [90].

The used laser systems are limited in there maximum output power. To still achieve comparable optical amplification above the optical breakdown threshold the focus spot size has to be reduced to about 1 \( \mu m \) in diameter. This can be achieved with high NA microscope objectives (NA = 0.4, 0.6) and results in intensities in the focal area of about \( I = 2.5 \cdot 10^{14} \text{ W/cm}^2 \) (\text{ @ } P_m = 0.6 \text{ W}, f = 500 \text{ kHz}, \tau = 500 \text{ fs}).

The earlier used microscope objectives are telecentric flat-field objectives. They provide a much smaller scan field since they were designed for other applications. Also, a sim-

\(^5\)Sill optics: telecentric f-theta lens S4LFT4031/126 with the smallest available focal length \( F = 32.8 \text{ mm} \) and a max. beam diameter \( A = 10 \text{ mm} \).
ple combination of a galvanometer scanner and microscope objectives results in an even smaller scanning fields and distortion since the exit pupil of the lens system is typically located several mm inside the microscope objective (see table 7.2). To overcome this issue the beam path between microscope objective and scanner is designed with a ray tracing program Zemax from Radiant Zemax (see section 7.2.2). To make up for the small scan field, at a later development stage a tile feature is implemented in the scanner software (see section 7.3).

In this work a hurrySCAN® II (fig. 7.5) is used. It is a compact scan head from SCAN-LAB for laser material processing available with different apertures from 7–14 mm. The scanner head with a 10 mm aperture (see Appendix A.5) provides the best compromise between marking speed and precision for this application. To supply the flexibility of using the set-up with different wavelengths the scanner is equipped with silver mirrors. The specifications, like precision, mark speed, positioning speed and scan field size of the scanner set-up (fig. 7.5)(in the following be called µScanner) depend mainly on the equipped microscope objectives. The size and location of the microscope objectives restrict the scan angle to about ± 0.04 rad (table 7.3).

For the communication between computer and scanner head, a RTC®4 PC interface board is used. The computer software (Scan2D) used to control the scanner head via the RTC®4 PC interface board is a CAD/CAM software programmed by Ortmann Digital-technik. The software is tailored for laser material processing of 2D geometries and is continuously improved during the construction of the µScanner. For instance, in early versions the translation stage axes are still controlled manually. Later on they are controlled through the scanner software. Moreover, Scan2D is used to control the laser beam (on and off ) via the AOM. The scanner head sends a TTL signal which is used to trigger the AOM.

Using an AOM becomes essential for laser marking. To achieve homogenous results constant marking velocities are required. The maximum velocity with which this can be done is denoted in table 7.3 as mark speed. During the positioning phase (not constant positioning speed) the laser beam is usually switched off. Once the job⁶ is completed, the scanner will send a signal to switch off the laser beam.

The µScanner is attached to the z-axis of the three axis positioning stage Microstep. Moving the µScanner along the z-axis, the laser focus is positioned in relation to the sample. In this stage of the development the translation axes are still controlled manually.

To view the sample surface while adjusting the sample position and for process control (automated process control might be integrated later) an imaging and illumination beam path (see section 7.2.3, 7.2.4) are added to the set-up.

<table>
<thead>
<tr>
<th>Microscope Objective</th>
<th>2ω₀ [µm]</th>
<th>Precision [nm]</th>
<th>Mark speed [mm/s]</th>
<th>Positioning speed [mm/s]</th>
<th>Øₚ scan field [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD Achroplan 20x</td>
<td>20x</td>
<td>430</td>
<td>103</td>
<td>360</td>
<td>1.2</td>
</tr>
<tr>
<td>LD Achroplan 40x</td>
<td>40x</td>
<td>210</td>
<td>51</td>
<td>180</td>
<td>0.6</td>
</tr>
<tr>
<td>LCPLN20X IR</td>
<td>20x</td>
<td>470</td>
<td>115</td>
<td>403</td>
<td>1.3</td>
</tr>
<tr>
<td>LCPLN50X IR</td>
<td>50x</td>
<td>190</td>
<td>46</td>
<td>161</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 7.3.: Specifications of the µScanner depending on the utilized microscope objectives.

---

⁶Job is the data format which contains the data for the irradiation of a 2D structure.
7.2.2. Laser Beam Path

For an optimal match of the scanner and the microscope objectives the laser beam path is designed with a ray tracing software, Zemax from Radiant Zemax. In the design a 1:1 telescope is used to image the exit pupil of the microscope objective onto the scanner mirrors. The beam path is optimized for minimal aberrations. The optical path between scanner and microscope objective is about 500 mm in length. To enable a compact design, the beam path is folded twice using 45° mirrors (fig. 7.5). The optical path is completely enclosed to protect optical elements from dust on the optical elements and for laser security reasons. The laser power is adjusted with a λ/2-plate and a polarizer before passing through

![Figure 7.5.](image)

**Figure 7.5.** Schematic of the optical path from the galvanometric scanner to the microscope objective. The purchased components are the hurrySCAN® II and the microscope objectives.

![Figure 7.6.](image)

**Figure 7.6.** Schematic of the set-up for the irradiation of 2D and 2½D structures on the surface and in the volume of the sample [108]. The imaging and illumination beam path are marked yellow and the laser beam path is marked green.
the AOM. Then, the laser beam is guided into the scanner using a 45° mirror with dielectric coating for the laser wavelength. The dielectric coated mirror is mounted in the illumination path transmitting also the LED light (fig. 7.6). However, the illumination beam still undergoes an off-set towards the laser beam when it passes through the 5 mm thick glass substrate of the mirror. Therefore, the laser beam and the illumination beam are not exactly overlapping. This increases the complexity when adjusting the laser beam into the μScanner. This is a tolerable problem which should be solved in a later version of the μScanner by integrating a compensation plate in the illumination path.

7.2.3. Imaging Path

A high speed camera MV-D1024E-160-CL12 from Photon Focus with a monochrome CMOS-chip is selected for imaging. The camera provides a high dynamic range of up to 120 dB at a resolution of 1024 x 1024 pixels. At full resolution, a maximum image rate of 150 frames per second is achieved. More frames per second are possible by reducing the frame size and reading out only a part of the sensor. Very little to no light is reflected by transparent materials and therefore contrast is already low. LinLog technology enables a high image contrast, required when working with transparent materials. The CMOS sensor has a spectral response in the visible and near infrared range (\(\lambda = 300 – 1000\) nm). The compact architecture (55 x 55 x 32 mm\(^3\)) and the low weight are further benefits of this camera. The camera has a C-mount to equip an objective or to be mounted onto a microscope. Together with a focussing objective the camera is coupled into the illumination path via a beam splitter (fig. 7.6).

A fast image data transfer between the camera and the computer is ensured by using the frame grabber Dalsa X64 XCELERA-CL PX4 Dual. Since the frame grabber provides 128 MB image memory, the computer CPU is not used and capturing many pictures does not affect the performance of the computer and scanner. This becomes very important when irradiating 3D geometries since these are sliced into 2D geometries, each stored in a files. The files are separately loaded into the scanner software.

7.2.4. Illumination Path

The illumination path is designed according to a Köhler illumination for a contrast rich and bright image. Köhler illumination ensures an even sample illumination while at the same time the image of the light source is not visible in the sample plane. A Köhler illumination consists of a light source, several imaging optics and two adjustable diaphragms. The light source is a high power LED Ostar®-Lighting by OSRAM which provides outstanding brightness and luminance. Light in the spectral range from \(\lambda \approx 400 – 750\) nm is emitted by the LED. The LED is mounted on an aluminum cooling plate to provide an appropriate heat exchange and maintain a long lifetime. The emitted radiation is directed using a collector lens and is then guided by field lenses and a condenser into the scanner.

The μScanner set up is attached to the z-axis of the positioning stage and the weight should be kept as low as possible (best below half of the maximum load of 20 kg) to maintain the precision of the axis.
The illumination path is designed and optimized for a homogeneous illumination of the exit pupil image of the microscope objective (located between the scanner mirrors). In the illumination path, the beam is restricted by a luminous-field diaphragm and an aperture diaphragm. The luminous-field diaphragm is used to adjust the size of the illuminated object field. Moreover, the diaphragm helps to minimize the scattered light in the beam path and therefore increase the contrast. The image plane of the luminous-field diaphragm coincides with the object plane while the aperture diaphragm coincides with the focus planes of the light source. The aperture diaphragm is used to control the angle of the light cone reaching the object. The NA of a microscope is defined by the size of the diaphragm and the microscope objective aperture. A widely opened diaphragm results in high numerical aperture and therefore high resolution but also weak contrast. The optimal size of the aperture diaphragm is defined by the best compromise between resolution and contrast.

The illumination path is about 300 mm. The optical elements are mounted in a cage system from Thorlabs. For the design and the optimization of the µScanner, a cage system is the best choice. It allows a high degree of flexibility regarding the positioning of the lenses while being very stable.

7.3. Adaptation for 3D Manufacturing Compatibility

For the fabrication of 2D geometries larger then the scan field diameter $\varnothing_s$ or for 3D geometries, e.g. cone, two improvements are implemented:

1. Implementation of the control of the positioning stage into the scanner software.
2. Adding software for the processing of 3D CAD models.

Large 2D geometries:
The implementation of the positioning stage control into the scanner software, Scan2D, is essential for the automated irradiation of large 2D and 3D geometries. Since the translation stage is an older model, its software and controller cards are not up to date and could not be brought up-to-date for various reasons. Therefore, the communication could not be established in the same way as it is done for newer models. To enable information exchange, a network interface card is built into the control computer of the positioning stage. Also the positioning stage’s LabVIEW-based control software is modified to receive commands from an external computer. Thereby, the movement of the positioning stage can be completely controlled through the scanner software.

Scan2D has a tile feature used to irradiate areas larger than the equipped microscope objective’s scan field diameter $\varnothing_s$. The desired geometry is imported as vector graphic, bitmap or simply created in Scan2D. The activation of the tile feature will divide the geometry into tiles with the desired tile size $a$ (fig. 7.7 right). The size of a square tile with the length $a$ is chosen to fit inside the scan field. The diagonal of the tile therefore equals the scan field diameter $((a^2 + a^2)^{1/2} = \varnothing_s)$ (fig. 7.7 left). The single tiles are processed by the galvanometric scanner in the labeled order with the adjusted writing speed $v$. After scanning the first tile, the scanner sends a signal to the AOM to switch off the laser beam.

\footnote{The optical path is designed using the ray tracing program Zemax.}
and a signal to the positioning stage to move the sample by a distance $a$ in $x$-direction. After positioning the sample, the translation stage sends a signal to initiate scanning the second tile. This signal triggers the AOM to switch the laser on and the scanner to start its program. Depending on the amount of tiles, the process chain is performed according to the example given in figure 7.8. The tiles are always irradiated from bottom left tile to top right tile.

When so many devices work together, all devices have to be harmonized. The translation plane of the axis is here taken as origin of the coordinate axis $(x, y, z)$. The scanner mirrors move the laser beam in the scan field plane $(x', y')$, perpendicular to the $z'$-axis of the scanner coordinate system. Without proper adjustment, both coordinate systems do not automatically superimpose (fig. 7.9 a).
Tile error:
When moving the sample for the irradiation of large 2D geometries in the x-y plane, it is important that the scan field is adjusted parallel to the translation plane (\(z = z'\)). If the scan field is tilted in relation to the translation plane the misalignment will lead to noticeable change in the irradiation result (see fig. 7.9 b). If the \(z'\)-axis of the scanner coordinated system (perpendicular to the scan field plane) and the z-axis of the positioning stage are tilted in relation to each other at an angle \(\gamma\), then the scan field is tilted at the same angle \(\gamma\) (fig. 7.9 a) left). In the example in fig. 7.9 b), an in-volume marking in a transparent sample, the misalignment becomes visible when white light is refracted by the grating irradiated in the sample. The tilt of the scan field is noticeable in the colour gradient (between lower left and upper right corner of a tile) of the interference pattern. Moreover, when irradiating the surface of a sample a tilted scan field can lead to abortion in the ablation. To avoid these problems the scan field is adjusted parallel to the translation plane (\(z = z'\)) (fig. 7.9 a) left). The adjustment is done manually using the 45° mirrors of the \(\mu\)Scanner (see fig. 7.5).

Contortion error:
After eliminating the tilt error (\(z = z'\)), the \(x'-y'\) plane of the scanner still can be contorted towards the x-y plane of the positioning stage (fig. 7.10 a). In this case, the scanner coordinate system is parallel to the coordinate system of the translation axis (z-axis are identical), but the x- and y- axis of both coordinate systems are not superimposed. The \(x'\)- and \(y'\)-axis of the scanner and the x- and y-axis of the translation stage enclose the angle \(\alpha\). It is difficult to avoid the contortion between both coordinate systems during the adjustment, but it is relatively simple to define the scanner coordinate system in the scanner software settings. The software supports the adjustment of the scan field angle \(\alpha\).
A non-corrected contortion error resembles itself in rotation of the tile around \(z'\)-axis. A
Figure 7.10.: a) Coordinate system of the translation stage (blue) and of the scanner (red) are contorted (left) with the angle \( \alpha \) between y- and \( y' \)-axis. b) Microscope image of contortion error \( \alpha = 2.73^\circ \) in an in-volume marking which results in an off-set of the tiles along the y-axis \( \Delta y = 11.5 \mu \text{m} \).

step in y direction is found when matching tiles (fig. 7.10 b). This step results from the additional translation axis movement between the irradiation of the single tiles.

Delay error:
During irradiation of a geometry, the laser is controlled by the scanner software. TTL signals (laser on, laser off) are sent from the scanner head to the AOM. The irradiation duration is defined by the laser on and laser off signals of the scanner. Since the signal requires a specific time to reach the AOM and the AOM also has a reaction time, the signal laser on is sent before the galvanometer mirrors start to move. The time between sending the laser on signal and the start of the mirror movement is the laser on delay. Accordingly, there is also a laser off delay.

Not well adjusted delays can result in incomplete irradiation (fig. 7.11). In the resulting marking, a delay error is recognized by either a too short or too long irradiated track.

Figure 7.11.: Schematic and microscope image of a delay error in an in-volume marking. The signal for laser on is sent too late, resulting in a too short laser on delay.

The example depicted here is a geometry filled with equidistant lines. To achieve this filling, the scanner mirrors are meandering the laser beam over the sample. During the movement, the laser is switched on by the laser on signal at the beginning of the writing phase (constant writing speed) in positive x-direction (fig. 7.11 left). When the end of the
7.3. Adaptation for 3D Manufacturing Compatibility

tile is reached the laser is switched off by a second signal from the scanner. The scanner mirrors are now positioning the focus spot (positioning phase: not constant positioning speed) in negative y-direction. Following the positioning, the laser is again triggered by a scanner signal (laser on) and the procedure is repeated in negative x-direction and so on. A problem occurs when the laser on/off delay is not adjusted correctly (too long/short) which will result in a late/early switched on/off of the laser beam. The delay error is corrected in the delay settings of scanner software.

At this development stage it is possible to irradiate large 2D geometries since the control of the positioning stage has been incorporated in the scanner software. This technical improvement also enables the irradiation of 3D geometries.

3D geometries:
To irradiate 3D geometries (here a cone) the irradiation process has to be broken down into 2D slices of the 3D CAD model (fig. 7.12). This process is called slicing. In this work, Rhinoceros® 4 from McNeel is used to import 3D CAD models in step-format (.stp) and export files with the 2D slices in SLC-format. During the export, the slice thickness is defined. The thickness should match the off-set in z-direction Δz and, in this work, is varied between 0.5 and 5 μm.

![Figure 7.12.: Schematic of the preprocess including dividing the 3D geometry into 2D geometries (slices) and creating a list of job-files for the rapid prototyping (RP) process.](image)

The SLC-format is then used with an additional program, Ablation Control by Ortmann Digittechnik, to create a list of job files (.job is the file format in which Scan2D saves the 2D geometries) with ascending number of the slices of the 3D geometry. Every job file contains the information for the irradiation of a x-y-plane in one defined z-position. The irradiation is initiated at the lowest z-position (job file with the lowest number) (fig. 7.12). After irradiating the first 2D geometry (1.job), the z-position for the irradiation of the second 2D geometry is automatically adjusted by the translation stage. In parallel, the second job file (2. job) is loaded into the scanner software. When the new z-position is adjusted, the second 2D geometry is irradiated, and so on.

By using the additional software (Rhinoceros, Ablation Control), it is possible to irradiate a 3D geometry with the μScanner in a layer-by-layer manner.

Workflow:
In this development stage the workflow for SLE (fig. 7.13) is very similar to other rapid prototyping techniques and consists of three steps: Preprocess, Rapid Prototyping Process (RP Process) and Post Process.
Preprocessing mainly includes the preparation of the job files for the scanner software from the 3D CAD model. In the RP process, the irradiation of the 3D geometry with the prepared data follows. In post processing, the irradiated areas are removed by etching the sample in an aqueous solution of HF acid. The result is either a 3D geometry which is removed from the sample or a sample with the remaining hollow geometry, e.g. bore hole, microfluidic channels or hollow volumes.

### 7.4. Conclusion and Outlook

The μScanner's (fig. 7.14) purpose is to irradiate 2D/3D geometries in transparent materials using femtosecond laser radiation focused to a spot size of about 1 μm. The optical paths of the laser beam, the imaging and the illumination are designed and optimized for minimal aberration and maximal performance. They match the specifications of the laser source, the galvanometric scanner, the microscope objectives, the high speed camera and the LED. The implementation of the μScanner with the positioning stage creates a tool not only for fast irradiation (up to 100 mm/s) with sub-μm precision, but also for the automated irradiation of large 2D geometries with sub-μm precision. With this first prototype of the μScanner, the scanning speed is increased by a factor of 50 compared to the positioning stage (from 2 mm/s to 100 mm/s).

![Figure 7.14.: μScanner with microscope objective and correction collar adjustment [108].](image)

The restriction of the workspace (≈ 1-2 mm), due to the small aperture of microscope objectives, is overcome by implementing a software to stitch small workspaces (tiles) to-
7.4. Conclusion and Outlook

together to a larger workspace. The maximum workspace diameter is given by the maximum translation stage range (150 mm). Also, the communication of the different hardware components amongst each other is solved to automate the irradiation of large 2D or complex 3D geometries. For this purpose, modified versions of Scan 2D and Ablation Control are used. These programs control the scanner, the laser and the translation stage. By implementing a CAD-CAM software, the preprocessing time is drastically reduced, especially for complex 3D geometries (see section 8.2.3 for examples). CAD models for 3D geometries are sliced by the CAD-CAM software, under given parameters, into 2D geometries representing single layers. The irradiation of the 3D geometry is afterwards conducted layer by layer. At this development stage, the \( \mu \)Scanner is a tool for prototyping or small batch series fabrication. Before the \( \mu \)Scanner can be implemented in industrial production, further improvements are required.

1. Autofocus/-adjustment
2. Automated process diagnostic
3. Automated precompensation of the spherical aberration

So far, the focus and sample adjustment are not automated. These require the implementation of some cylindric lenses into the beam path and a programmed logic for the automated adjustment of the sample and the focus. Also, it would be beneficial to implement an automated process diagnostic to avoid cracks, or at least, to detect crack formation and not properly irradiated areas. The high frame rate of the CMOS-camera and the high resolution due to the Köhler illumination already provide the hardware requirements for this diagnostics process. The required software is not addressed as part of this thesis.

Working in different depths of the material leads to spherical aberrations. The used microscope objectives are equipped with a compensation collar for manual precompensation of the spherical aberration (SA). It is inefficient to manually compensate the SA for every depth during irradiation since the irradiation process has to be stopped for every compensation adjustment. Moreover, it is not completely understood how increasing SA would influence the SLE process and the surface qualities of the final components. The focus in this work is to investigate the effect of the different SAs on the surface quality and finding a process window where the SA might not affect the final result. Nevertheless, the hardware components for a automated compensation of the SA are implemented into the \( \mu \)Scanner. Adequate adapter rings with correct gear ratio to match a brushless DC-servomotor with integrated motion control (3564K024BCS) from Faulhaber are designed for each microscope objective. A software to adjust the SA by turning the correction collar, while adjusting the height of the next layer has not yet been implemented.

Further improvements can be achieved by integrating the \( \mu \)Scanner with a newer model positioning stage. For instance Aerotech provides translation stages with speeds up to 300 mm/s. Thereby, the positioning time in the tile modus would be decreased. Moreover, coordinating the communication between \( \mu \)Scanner and positioning stage may be much easier and even allow "on the fly operation" \(^9\).

\(^9\)Scanner and positioning stage work at the same time, which leads to a reduction of dead time.
Chapter 8.

Process Development

In this section, the individual steps of the process development of SLE are displayed. The requirements for the process development for 3D geometries are the driving force for the μScanner development. For the proof of principle (see section 8.1) the simple lab setup described in section 7.1 is used. The general feasibility is proven by testing different irradiation and etching parameters on a simple microchannel geometry. Moreover, the crystalline structure and the defect formation are investigated.

The results from the investigation of microchannels are used in section 8.2 for the irradiation of overlapping microchannels (in x-y plane and z-direction). This irradiation strategy creates hollow volumes and cuts as well as 3D components in 2½D geometry, e.g. cylinders and cubes. In addition to the investigation of the laser induced stress, the process window is investigated. In this section, the μScanner is used for the first time to irradiate 2½D geometries. Moreover, the feasibility of ruby as a material for SLE is demonstrated.

The irradiation of 3D devices in 3D geometry is exemplarily conducted on a cone to demonstrate the functionality of the μScanner and the CAD-CAM software (see section 8.3). With the irradiation of 3D geometries, many new irradiation possibilities and parameters are connected. It is impossible to investigate the complete process window within the scope of this thesis. Nevertheless, the irradiation of a cone demonstrates that the μScanner is fully able to irradiate of 3D geometries.

8.1. Process window for 2D Geometries

SLE is a two-step process consisting of the irradiation and etching steps. The influence of all process parameters is investigated. All adjustable laser parameters and the irradiation speed are the topics of section 8.1.1. The influence of the focusing, including the SA, is investigated in section 8.1.2. Different acid concentrations and different etching times are investigated in section 8.1.3. Since the foundation for a process development is a good understanding of the process itself the change in crystalline structure is investigated using EDX and Raman spectroscopy. Both are less expensive alternative to transmission electron microscopy (TEM) investigation (section 8.1.4). Furthermore, crack formation in relation to different process parameters is investigated (section 8.1.5) since cracks limit the process window of SLE.

For all investigations in this section, microchannels are generated from a single irradiated track. To irradiate the tracks, laser radiation is tightly focused in a depth \( d \) inside the sample while the sample is moved with a velocity \( v \) in the x-y-plane (perpendicular to the
inclining laser radiation) (fig. 8.1). The laser radiation is linearly polarized. Subsequently, the irradiated, and therefore modified, material (in the following also called modification) is removed by etching the sample in acid (see section 8.1.3).
For the experiments, single crystalline sapphire samples with the dimension 10 x 10 x 1 mm$^3$ are used. The c-axis of the crystalline structure is aligned in z-direction (along the 1 mm long edge) and therefore the laser radiation is parallel to the c-axis.

![Diagram of a microchannel](image)

**Figure 8.1.** Schematic of irradiated microchannel in a depth $d$ and alignment inside the sample.

The lines are irradiated in y-direction, perpendicular to the polarization of the laser radiation. This irradiation direction is chosen because Hnatovsky has shown the existence of a polarization dependency of the etching rate in fused silica [109]. This polarization dependency is caused by self-organizing periodical nanostructures, so-called nanoplanes, formed under the influence of ultrashort pulsed laser irradiation. Nanoplanes are oriented perpendicular towards the polarization of the laser radiation. Since nanoplanes also form in sapphire it is assumed that the same polarization dependent etching rate exists. Therefore, it is important to keep the orientation of the laser polarization towards the scanning direction the same for every experiment.

After the irradiation, the samples are lapped from both sides (perpendicular to the scanning direction, fig. 8.1) to remove the irregular irradiated areas. Due to diffraction and reflection from the sample’s edges, the irradiation is not consistently close to the edge (see A.9). In this way, locally reduced etching, due to irregular irradiation, is removed. All samples were lapped on a Logitech PM-5 lapping and polishing machine by using a lapping agent (silicon carbide) with a grain size of approximately 9 µm.

Afterwards, the sample is etched in HF-acid. The concentration $c$ of the aqueous solution of HF-acid is 48% for all experiments conducted in this section unless indicated otherwise. Also, the etching duration $t$ is kept constant at $t = 24h$ unless indicated otherwise.

### 8.1.1. Irradiation

In this section, the influence of parameters, like pulse energy $E_p$, irradiation speed $v$ and the number of passes $#n$ on the dimensions of the microchannels formed after etching is investigated. The dimensions inspected for this validation are the microchannel length $y$ and the cross section length $z$ and width $w$ (fig. 8.2). For the measurement of the microchannel length $y$, optical microscopy (see section 6.1) is utilized while for the cross section dimensions $z$ and $w$ SEM (see section 6.3) is used (fig. 8.3). The irradiation of the single tracks is conducted in positive as well as in negative y-direction. The indicated
8.1. Process window for 2D Geometries

Figure 8.2.: Schematic of microchannels with a length $y$ and cross section width $w$ and length $z$ after etching. The channels are irradiated along the $y$-axis with the speed $v$.

![Schematic of microchannels](image)

Figure 8.3.: Microscopy image of microchannels irradiated in $\pm y$-direction after etching. The channel length $y_+$, $y_-$ (left) is indicated (left). SEM image of a channel cross section with indicated width $w$ and length $z$ (right).

![Microscopy image](image)

pulse energy $E_p$ is measured before the sample. Therefore, a system independent value is displayed, after the microscope objective, µScanner and other optics.

**Pulse energy:**
To investigate the influence of the pulse energy $E_p$ on the formation of microchannels, the following processing parameters are used (tab. 8.1).

<table>
<thead>
<tr>
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</tr>
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<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>24</td>
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<tr>
<td>0.6</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>24</td>
<td>0.15 – 0.9</td>
</tr>
</tbody>
</table>

**Table 8.1.:** Process parameters for microchannel ($c$: concentration of HF-acid, $t$: etching duration)

**Channel length $y$ versus pulse energy $E_p$:**
The plot of the measured channel length $y$ versus used pulse energy $E_p$ (fig. 8.4) reveals that the channel length $y$ is not dependent on the pulse energy. Instead a difference in channel length between negative and positive irradiation direction ($\pm y$) is observed. The difference in channel length is especially significant for channels irradiated with NA = 0.6 (green/blue lines) ($\Delta y_{+/-} \approx 300$ µm). For NA = 0.4, the difference in channel length
Figure 8.4.: Etching length \( y \) is independent of the pulse energy \( E_p \) but dependent of \( \pm y \)-direction and the NA (0.4, 0.6) with (corr, dashed line) and without (solid line) precompensation of SA (irradiation depth \( d = 500 \mu m \), \( f = 500 \) kHz, \( c = 48 \% \) HF, \( t = 24 \) h).

between \( +y \) and \( -y \)-direction exists but is only about \( \Delta y \approx 50 \mu m \). The reason for the dependency of the channel length \( y \) on the irradiation direction might be caused by a pulse front tilt of the laser radiation. Kazansky et al. first reported the phenomena of the variation in formed nanostructures depending on the irradiation direction in 2007 [110]. He assigns his investigations to the existence of a pulse front tilt which, very likely, exists when using femtosecond laser radiation. In 2008, he indirectly proved the influence of the pulse front tilt on the change in formation of nanostructures by purposefully changing the pulse front tilt of his set up [111]. These results were followed by further investigations [112] on the influence of the pulse front tilt, leading to similar results to those found in this work (dependency of the microchannel cross section length \( z \) and width \( w \) on the irradiation direction \( \pm y \) (fig. 8.5, 8.6).

Another process parameter by which the channel length \( y \) is influenced is the SA. Microchannels irradiated without precompensation for SA in an irradiation depth \( d = 500 \mu m \) reveal a smaller channel length. For microchannels irradiated with NA = 0.6, the effect of the SA is more significant than for NA = 0.4. Microchannels irradiated (NA = 0.6) with precompensation of the SA (corr) (dotted line) are about \( \Delta y = 400 \mu m \) longer than microchannels irradiated without precompensation (solid line). This finding is independent of the irradiation direction (\( \Delta y_+ = \Delta y_- \)). The irradiation with NA = 0.6 results in up to 1400 \( \mu m \) long microchannels, which is about 1000 \( \mu m \) longer than with NA = 0.4. The drawback is that precompensation of SA is required for NA = 0.6.

For NA = 0.4 the influence of SA on the channel length is not visible for the irradiation depth of 500 \( \mu m \). Therefore, the precompensation of SA is not required for small numerical apertures like NA = 0.4 which minimizes the irradiation effort when irradiating at different depth.

In addition, it is well visible that the channel length \( y \) is split into two regimes depending on the NA. With NA = 0.4 channels with a length of 300 - 600 \( \mu m \) are generated. Using
NA = 0.6, on the other hand, results in channels with a length between 500 - 1400 µm.

**Channel width w/length z versus pulse energy $E_p$:**
The cross section width $w$ and length $z$ are both increasing with the pulse energy $E_p$. The dependency of the cross section dimensions $w$ and $z$ from the pulse energy is plotted in fig. (8.5, 8.6).

![Graph showing the relationship between cross section width $w$, energy $E_p$, and NA (0.4, 0.6).](image)

**Figure 8.5.:** Cross section width $w$ is increasing with pulse energy $E_p$ for ± y-direction and two different NA (0.4, 0.6) with and without precompensation of the SA (irradiation depth $d = 500$ µm, $f = 500$ kHz, $c = 48$ % HF, $t = 24$ h).

![Graph showing the relationship between cross section length $z$, energy $E_p$, and NA (0.4, 0.6).](image)

**Figure 8.6.:** Cross section length $z$ linearly increases with pulse energy $E_p$ for ± y-direction and two different NA (0.4, 0.6) with and without precompensation of the SA (irradiation depth $d = 500$ µm, $f = 500$ kHz, $c = 48$ % HF, $t = 24$ h).
Chapter 8. Process Development

The cross section dimensions are influenced by the scanning direction and the SA for both NAs. Similar to the microchannel length for each NA, a regime is found in which the channel width or length varies. For the channel width, the regime of the NA = 0.4 and NA = 0.6 overlap in the middle. The channels in the overlapping regime are mainly generated with precompensation of SA, whereas the microchannels in the not overlapping regime are mainly generated without precompensation of SA. Irradiation with NA = 0.4 results in wider microchannels than irradiation with NA = 0.6. The process window for NA = 0.6 (with precompensation of SA) is larger which results from focusing to a smaller focal area $A = \frac{\pi \omega_0^2}{4}$ with $\varnothing_f = 2\omega_0^1$. The intensity distribution in a Gaussian beam is proportional to $\propto E^2$ and therefore the energy required for an optical breakdown is lower with higher NA (stronger focusing = smaller focal spot size).

For the cross section length $z$, the influence of the irradiation direction is large for NA = 0.4 and results in a range of cross section length $\Delta z \approx 37 \mu m$ for one pulse energy. For NA = 0.6, the range in cross section length is $\Delta z \approx 14 \mu m$. For both NAs, the cross section length $z$ inclines linearly with pulse energy $E_p$ at a gradient of $\frac{\Delta z}{E_p} = 37.5 \mu m/\mu J$. Concluding, it is noticed that the channel length $y$ does not depend on the pulse energy $E_p$ but it is influenced by NA, SA and irradiation direction $\pm y$. NA = 0.6 results in longer microchannels and benefits greatly from precompensation of the SA. The cross section width $w$ and length $z$ increase with increasing pulse energy $E_p$. The influence of the irradiation direction and of the SA are visible as well. The influence of the irradiation direction $\pm y$ on the resulting microchannel requires more investigation since it has a major influence on all measured microchannel dimensions. The SLE process might benefit greatly from the possibility of adjusting the pulse front tilt for the laser-scanner system. SA is a parameter which has to be controlled/precompensated for numerical apertures above 0.4.

Irradiation speed:
To investigate the influence of the irradiation speed $v$ on the formation of the microchannel and their dimensions, a positioning stage from Aerotech with a max irradiation speed $v = 300 \text{ mm/s}$ is used instead of the positioning stage from Kugler (max irradiation speed $v = 2 \text{ mm/s}$). Microchannels are irradiated with $v = 2 - 150 \text{ mm/s}$ for different numerical apertures (NA = 0.4, 0.6) with precompensation of the SA (corr) and for different irradiation directions $\pm y$. The pulse energy is kept constant at $E_p = 0.64 \mu J$ (table 8.2).

<table>
<thead>
<tr>
<th>NA</th>
<th>$d$ [\mu m]</th>
<th>$f$ [kHz]</th>
<th>$E_p$ [\mu J]</th>
<th>$c$ [%]</th>
<th>$t$ [h]</th>
<th>$v$ [mm/s]</th>
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<td>2 – 150</td>
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<td>- 500</td>
<td>500</td>
<td>0.65</td>
<td>48</td>
<td>24</td>
<td>2 – 150</td>
</tr>
</tbody>
</table>

Table 8.2: Process parameters for microchannel ($c$: concentration of HF-acid, $t$: etching duration)

The plot of the channel length versus the irradiation speed reveals limited growth of the channel length $y$ with increasing scanning speed $v$ for both numerical apertures

$p^1$The focal spot size for the NA of 0.4/0.6 is under ideal conditions, in air, without SA, $2\omega_0 = 1.66/1.11 \mu m$. 

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Figure 8.7.: Channel length $y$ increases with the scanning speed $v$ for $\pm y$-direction and two different NA (0.4, 0.6) with precompensation of the spherical aberration until reaching an maximum at $v_{opt}$ (pulse energy $E_p = 0.64 \mu J$, irradiation depth $d = 500 \mu m$, $f = 500 \text{ kHz}$, $c = 48 \%$ HF, $t = 24 \text{ h}$).

(0.4, 0.6) and both scanning directions ($\pm y$-direction). Microchannels irradiated with NA = 0.6 show the maximum channel length ($y \approx 1500 \mu m$) from $v_{opt} = 100 - 150 \text{ mm/s}$. The difference in channel length $\Delta y$ at $v = 2 \text{ mm/s}$ and the maximum value $v_{opt}$ is $\Delta y_{+,/-} = 200/470 \mu m$ for NA = 0.6.

Microchannels irradiated with NA = 0.4 reveal the same relation between channel length $y$ and irradiation speed $v$. The growth of the channel length with the increasing irradiation speed is even larger than at higher numerical aperture. The difference between the channel length $\Delta y$ at $v = 2 \text{ mm/s}$ and $50 \text{ mm/s}$ is $\Delta y_{+,/-} = 850/900 \mu m$ for positive/negative $y$-direction. The optimum scanning speed range is $v_{opt} = 50 - 150 \text{ mm/s}$ (NA = 0.4).

The cross section length $z$ and width $w$ do not reveal a dependency on the scanning speed $v$ (fig. 8.8). Therefore, it is possible to increase the length of the microchannel $y$ without changing the dimensions of the cross section by increasing the scanning speed to $v_{opt} = 50 - 150 \text{ mm/s}$ (NA = 0.4) and to $v_{opt} = 100 - 150 \text{ mm/s}$ (NA = 0.6).

The reason for the correlation between the channel length $y$ and the irradiation speed is not understood and has to be further investigated. It is assumed though that a heat/energy distribution effect might lead to recrystallization or increased defect formation at low irradiation speed. Already Juodkazis mentioned that multiple irradiations of the same location reduces the etchability due to recrystallization [12]. Multiple irradiations of the same location is equal to a pulse overlap of 100 %. At an irradiation speed of $v = 2 \text{ mm/s}$ with a repetition rate $f = 500 \text{ kHz}$ the pulse overlap is approximately 100%. At $v = 50 \text{ mm/s}$ the pulse overlap is reduced to about 94%/91% (NA = 0.4/0.6).

**Number of passes:**
A group at the Fraunhofer Institute in Freiburg created microchannels in sapphire using
Figure 8.8.: Cross section length \( z \) (dotted line) and width \( w \) (dashed line) are independent of the scanning speed \( v \) for \( \pm y \)-direction and two different NA (0.4, 0.6) with precompensation of the spherical aberration (corr) (pulse energy \( E_p \) = 0.64 µJ, irradiation depth \( d \) = 500 µm, \( f \) = 500 kHz, \( c \) = 48 % HF, \( t \) = 24 h).

ultraviolet picosecond laser radiation (10 ps) with a similar set up like described in (7.1). For focusing, a lens with a focal length \( F \) = 10 mm was used. The microchannels were irradiated in a depth \( d \) = 30 µm with an irradiation speed of \( v \) = 4 mm/s. For etching, a concentration of 40% HF-acid was used for different etching durations. The results of multiple irradiations on one microchannel revealed a decrease of the standard deviation in the microchannel length \( y \) with increasing number of passes \( n \) [102]. The standard deviation of the channel length (in % of the channel length) was reduced from 29.5 % at \( n = 1 \) to 2.2 % for \( n = 3 \) at the same pulse energy.

The results achieved with picosecond lasers could not be supported by the experiment conducted in this work with femtosecond laser radiation (for more details see appendix A.10). In agreement with the measurements with multiple passes and smaller NA (0.4), no dependency of the standard deviation from the number of passes is found. Nevertheless, a slight increase in channel length \( y = 30 \) - 70 µm is found up to \( n = 3 \) passes for microchannels irradiated with NA = 0.4/0.6. More than \( n = 3 \) passes result in a decreased channel length for NA = 0.3 and do not affect the channel length for NA = 0.6.

Repetition Rate:
To investigate the dependency of the channel length \( y \) on the repetition rate \( f \), samples are irradiated with the following parameters (table 8.3).

The compared samples (fig. 8.9) were irradiated with slightly different irradiation speeds \( (v = 1 \) mm/s, \( v = 2 \) mm/s). As shown earlier, higher irradiation speed results in longer microchannels. This dependency is visible when comparing microchannels irradiated with \( f = 500 \) kHz (black squares) (fig. 8.9). The small difference in irradiation depth between the two samples \( (d = 200 \) µm, \( d = 150 \) µm) should not have an influence on the microchannel length \( y \) since the SA is precompensated for both depths. The difference in channel length \( y \) irradiated with different repetition rates is not large and max about
Table 8.3.: Process parameters for microchannels (c: concentration of HF-acid, t: etching duration)

<table>
<thead>
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</thead>
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<td>200</td>
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<td>48</td>
<td>24</td>
<td>0.15 - 0.9</td>
<td>200, 500</td>
</tr>
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<td>1</td>
<td>48</td>
<td>24</td>
<td>0.15 - 0.9</td>
<td>100, 500</td>
</tr>
</tbody>
</table>

Figure 8.9.: Channel length $y$ versus pulse energy $E_p$ for $+y$-direction, different repetition rates ($f = 100$ kHz, 200 kHz, 500 kHz) and NA (0.6) with precompensation of the spherical aberration. (irradiation depth $d = 150 \ 200$ μm, $c = 48\%$ HF, $t = 24$ h).

$\Delta y = 100$ μm (for $f = 500$ kHz and $f = 200$ kHz). Higher repetition rates $f = 500$ kHz result in longer channel length $y$. The irradiation of microchannels with $f = 1$ MHz (not shown here) results in even larger channel length $y$. With the utilized laser system, the process window for the generation of microchannels is small at $f = 1$ MHz since the pulse power at this repetition rate is low. Therefore, for most of the experiments a repetition rate of $f = 500$ kHz is chosen. In addition a repetition rate of 500 kHz allows a higher irradiation velocity at high pulse overlap than a repetition rate of 100 kHz.

Conclusion:
The length of the microchannels $y$ highly depends on the used microscope objective (NA). With NA = 0.6 microchannels up to $y = 1400$ μm are fabricated at $v = 2$ mm/s and precompensation of the SA. The precompensation of the SA is essential for high NAs. Not precompensating the SA for NA = 0.6 results in a reduction of the microchannel length of about 400 μm. Microchannels irradiated with NA = 0.4 have a maximum channel length of about $y = 500$ μm at $v = 2$ mm/s. The influence of the SA for NA = 0.4 is almost immeasurable on the channel length and does not require precompensation.

For both NAs, the pulse energy $E_p$ has no influence on the channel length $y$. But the cross section width $w$ and length $z$ increase linearly with the pulse energy $E_p$. Moreover, the microchannel length $y$ increases with increasing irradiation speed $v$. Especially for microchannels irradiated with NA = 0.4, an increase in channel length of $\Delta y = 900$ μm
to a total channel length of \( y = 1300 \, \mu\text{m} \) is achieved using irradiation speeds above \( v = 50 \, \text{mm/s} \).

Using multiple passes while irradiating the microchannel does not reveal a major benefit in reducing the standard deviation of the channel length. Nonetheless \# = 3 passes reveal the best results in channel length for both NAs. Compared to the increase in channel length \( y \) due to increased irradiation speed the increase and therefore the benefit of multiple passes is neglectable. The influence in channel length due to changing irradiation direction \(+/-y\) reveals a by far larger standard deviation than the number of passes.

Microchannels generated with high repetition rates result in longer channels. Since the pulse power decreases with increasing repetition rate, for the used laser system, the highest repetition rate which is used is \( f = 500 \, \text{kHz} \).

Due to the current results, an increase in irradiation speed of up to \( v = 50/100 \, \text{mm/s} \) (NA = 0.4/0.6) is the most important process parameter to generate microchannel with a length of more than 1 mm.

### 8.1.2. Focusing

As soon as the laser beam is focussed inside a transparent material, the effect of spherical aberration (SA) on the formation of microchannel has to be taken into account. In section 5.2, the theory of the influence of SA on the focus shape is presented, but how this influences the formation of microchannels is not yet fully investigated.

In this section, the effects of SA on microchannels are closely investigated using microchannels irradiated with NA = 0.4 and 0.6 at different irradiation depths \( d \) and for different precompensation settings for the SA.

![Figure 8.10: Schematic of the irradiation strategy for microchannels in different irradiation depth \( d \).](image)

The parameters used for the generation of the microchannels are listed in table 8.4 and the irradiation strategy is depicted in figure 8.10. Moreover, the impact of the SA on the cross section shape (length \( z \), width \( w \)) of the microchannels is investigated. The cross section length \( z \) and width \( w \) are important parameters for the irradiation of 2D geometries since they define the distance, later called off-set, between different microchannels (section 8.2).

**NA = 0.6:**
For microchannels irradiated with NA = 0.6 with (corr) and without precompensation of
8.1. Process window for 2D Geometries

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</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>48</td>
<td>100 - 900</td>
<td>0.52, 0.78, 1.04, 1.3</td>
</tr>
<tr>
<td>0.6</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>6</td>
<td>100 - 900</td>
<td>0.2, 0.27, 0.34, 0.41</td>
</tr>
</tbody>
</table>

Table 8.4.: Process parameters for microchannel (c: concentration of HF-acid, t: etching duration)

SA, the channel length $y$ decreases (see fig. 8.11). Since the decrease in channel length $y$ is more rapid when SA is not precompensated, the difference in length $\Delta(y_{corr}, y)$ between microchannels irradiated with (corr) and without precompensation of SA increases with increasing irradiation depth. For irradiation depth $d = 100$ µm, a difference in channel length $\Delta(y_{corr}, y) \approx 50 - 100$ µm is observed. At $d = 500$ µm, this difference increases to $\Delta(y_{corr}, y) \approx 220 - 400$ µm, depending on the pulse energy used. For all investigated pulse energies, no microchannels irradiated uncompensated are found for irradiation depths $d > 600$ µm. This finding is appointed to the change in focal spot size due to SA. SA leads to an elongation of the focal spot size along the irradiation direction ($z$). Since the pulse energy remains unchanged, this results in a decreased intensity in the focal volume. If the intensity in the focal volume decreases below the intensity for optical breakdown, the material is no longer modified and therefore no microchannel is formed by etching.

As expected, the focus shape becomes more elliptic with increasing irradiation depth $d$,

![Graph showing channel length $y$ versus irradiation depth $d$ for different pulse energies ($E_p = 0.2, 0.27, 0.34, 0.41$ µJ), NA = 0.6, with and without precompensation of SA. The irradiation is not only conducted for one irradiation direction, but intermixed for y/x-direction ($f = 500$ kHz, $c = 48\%$, $t = 6$ h).]

**Figure 8.11.:** Channel length $y$ decreases with increasing irradiation depth $d$ for different pulse energies ($E_p = 0.2, 0.27, 0.34, 0.41$ µJ), NA = 0.6, with and without precompensation of SA. The irradiation is not only conducted for one irradiation direction, but intermixed for y/x-direction ($f = 500$ kHz, $c = 48\%$, $t = 6$ h).

due to increasing SA. When investigating the microchannel cross section dimensions $z$ and $w$ this is found when not precompensating the SA. The results are displayed in graph (fig. 8.12) as ratio of channel length $z$ over channel width $w$. For a non-precompensated SA, the ratio $z/w$ doubles between $d = 100$ µm and $d = 800$ µm, caused by an elongated cross section length $z$.  

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Figure 8.12.: Cross section ratio $z/w$ versus irradiation depth $d$ for different pulse energies ($E_p = 0.2, 0.27, 0.34, 0.41 \, \mu J$), NA = 0.6, with and without precompensation of SA. The irradiation is not only conducted for one irradiation direction, but intermixed for $-y/y$-direction ($f = 500 \, \text{kHz}$, $c = 48\%$, $t = 6 \, \text{h}$).

Even with precompensation for SA, a slight increase in $z/w$ is found with increasing irradiation depth $d$. Therefore, it is expected that the intensity in the focus volume is reduced as well. The reason for decreasing intensity might be found in either improper precompensation of SA or increased laser light scattering while propagating through the material. Further investigations, e.g. measuring the losses of the pulse energy when irradiating in different depths, are required to properly explain these results.

Figure 8.13.: Optical microscope image of etched microchannels ($c = 48 \%$, $t = 24 \, \text{h}$) irradiated in $d = 500 \, \mu \text{m}$ ($E_p = 0.36 \, \mu \text{J}$, $f = 500 \, \text{kHz}$) with NA = 0.6 and precompensation of SA for the depth $d_{corr}$.

To reveal how the cross section shape of the microchannels is influenced by different pre-
compensation conditions, six microchannels are irradiated with NA = 0.6 at a depth of d = 500 µm using a pulse energy of $E_p = 0.36$ µJ. The depth $d_{corr}$ in sapphire, for which the SA is precompensated, is indicated in the top right corner of figure 8.13. The shape of a microchannel cross section at depth $d = 500$ µm without precompensation ($d_{corr} = 0$ µm) (fig. 8.13 a)) is elongated ($z = 13.9$ µm) and has a width of $w = 1.8$ µm resulting in a ratio $z/w = 7.7$. The closer the precompensation depth $d_{corr}$ is to the irradiation depth $d = 500$ µm, the smaller is the cross section ratio $z/w$. With precompensation at depth $d_{corr} = 580$ µm (fig. 8.13 c)), the ratio $z/w = 3.7$ is minimal. Comparing this cross section ratio $z/w$ to the ratio of the double Rayleigh length $2z_R$ and focus diameter $2\omega_0$ for the used microscope objective (NA = 0.6: $2z_R/2\omega_0 = 3.4$) reveals that the values are very similar. Therefore, it is assumed that the precompensation is almost optimal. With precompensation for SA for depths larger than $d_{corr} > 500$ µm (overcompensation), the cross section ratio $z/w$ is increased again. Even with very strong overcompensation, the cross section length $z$ remains smaller than without precompensation for SA. In addition, the cross section cuts reveal a smooth, crack-free morphology. The reason for these findings is not yet clear. Further investigations of the laser focus and the intensity distribution in the focal area while focusing inside a material might lead to an explanation of this phenomenon, but will not be conducted in this work. Only the effect of overcompensation with NA = 0.4 will be investigated.

**NA = 0.4:**

Manually adjusting the correction collar for every irradiation depth is not feasible when moving the laser beam continuously in z direction. For a microscope objective with NA = 0.4, the continuous adjustment of the correction collar might not be required since the influence of SA is smaller than for NA = 0.6.

To verify this theory, microchannels irradiated with various SA precompensations are compared. In addition to microchannels irradiated with and without precompensation, microchannels irradiated with overcompensation for SA are investigated. The overcompensation is set for the lowest irradiation depth, here $d = 1000$ µm, and will be referred to as bottom corr (see fig. 8.14).

Comparing microchannel length $y$ irradiated with different SA settings, reveals that for NA = 0.4 an overcompensation for SA (bottom corr) results in longer channels than the precompensation at other depth. For a pulse energy $E_p \approx 0.7$ µJ (green), a difference in channel length of about $\Delta y_{bottomcorr-corr} \approx 100 – 200$ µm is observed (fig. 8.14). The channel length $y$ for all other pulse energies $E_p$ follows this trend. Investigating microchannel cross section ratios, $z$ and $w$, for different SA compensations settings (bottom corr, corr, without) (fig. 8.15) reveal differences between NA = 0.4 and NA = 0.6. Unlike NA = 0.6, the ratios $z/w$ for NA = 0.4 with (corr) and without SA precompensation remain between 19 and 9 at every irradiation depth. The cross section ratio $z/w$ for depth $d = 1000$ µm (bottom corr) also falls within the same range. Only the channel length $y$ increases, when overcompensating the SA for NA = 0.4.

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2Continuous adjustment was tested by using a motorized adjustment collar. The utilized electric motor was not free from slight vibrations which lead to movements of the focus in the µm-range. With a focal spot size of 1-2 µm this is not acceptable since it results in discontinuous irradiation. A piezo based adjustment of the correction collar might be better suited but is not tested in this work.
Figure 8.14.: Channel length $y$ versus irradiation depth $d$ for different pulse energies ($E_p = 0.43/0.41, 0.69/0.71, 0.87/0.86$ μJ), NA = 0.4, with, without precompensation of SA and with precompensation of SA in a depth of $d = 1000$ μm. The irradiation is not only conducted for one irradiation direction, but intermixed for $-/+y$-direction ($f = 500$ kHz, $c = 48\%$, $t = 6$ h).

Figure 8.15.: Cross section ratio $z/w$ versus irradiation depth $d$ for pulse energies $E_p \approx 0.67, 0.77$ μJ, NA = 0.4 with (corr), without precompensation of SA and with compensation of SA in a depth of $d = 1000$ μm (bottom corr). The irradiation is not only conducted for one irradiation direction, but intermixed for $-/+y$-direction ($f = 500$ kHz, $c = 48\%$, $t = 6$ h).

Conclusion:
Using NA = 0.6 with various SA precompensations the microchannel widths range from $w = 1 - 4.3$ μm and the channel length from $z = 9.6 - 13.9$ μm at a depth of $d = 500$ μm. To fabricate $2^{1/2}$D geometries, an off-set between adjacent focus positions (see fig. 8.16) in
z-direction should be smaller than the minimum focus length (fig. 8.13 c)) $\Delta z < 9.6 \, \mu$m.

![Schematic of microchannel off-set $\Delta z$ in z-direction and $\Delta x$ in x-direction.]

Figure 8.16.: Schematic of microchannel off-set $\Delta z$ in z-direction and $\Delta x$ in x-direction.

The off-set in x-direction between adjacent focus positions should be smaller than the channel width $w$ of a microchannel irradiated with SA precompensation $\Delta x < 2.6 \, \mu$m. For $\mathrm{NA} = 0.4$ the off-set value in z- and y- direction should be smaller than $\Delta z < 30 \, \mu$m and $\Delta x < 2.4 \, \mu$m. These values are extracted from the minimal cross section length/width of microchannel irradiated with precompensation of SA in a depth of $d = 1000 \, \mu$m (fig. 8.15).

For a closer investigation of the off-set between adjacent laser foci for the fabrication of $2^{1/2}$D geometries see chapter 8.2. For a qualitative comparison of microchannel cross sections generated with NA from 0.3 to 0.8 and the findings in literature see Appendix A.11.

### 8.1.3. Etching

The irradiated and modified sapphire volume is removed by etching the sample in an aqueous solution of hydrofluoric (HF) acid. Since crystalline sapphire is not etched by HF acid, the non-irradiated areas remain unaffected while the modified areas are removed by the acid, leaving behind microchannels in the volume.

For the etching, a closed container with a customized sample holder (fig.8.17), both made of Teflon, are used. The samples are mounted in the sample holder, enabling full contact between acid and modified areas. The container is placed in an ultrasonic bath filled with water for the whole etching time. The ultrasonic waves agitate the acid within the microchannels to prevent local reduction of the acid concentration $c$. Due to the energy induced by the ultrasonic waves, a temperature of approximately 60 – 70°C is obtained after about 1 – 2 hours. This temperature remains constant for the rest of the etching.
duration \( t \).

The objective is to find optimal etching parameters for a stable etching process. Therefore, the microchannel length \( y \) and the cross section dimensions, length \( z \) and width \( w \), are observed for different etching durations \( t \) and acid concentrations \( c \). The investigation is performed for different pulse energies \( E_p \).

**Etching duration:**

Samples irradiated with different pulse energies \( E_p \), using the parameters in table 8.5. Samples are then exposed for four different durations \((t = 6h, 24h, 30h, 48h)\) to an aqueous solution of HF-acid with an initial concentration \( c = 48\% \).³

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<thead>
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<th>( f ) [kHz]</th>
<th>( v ) [mm/s]</th>
<th>( c ) [%]</th>
<th>( t ) [h]</th>
<th>( E_p ) [µJ]</th>
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<td>48</td>
<td>6, 24, 30, 48</td>
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</table>

**Table 8.5.** Process parameters for microchannels \((c: \text{concentration of HF-acid, } t: \text{etching duration})\)

The resulting microchannel dimensions \( y, z \) and \( w \) are plotted versus the pulse energy \( E_p \) for different etching durations \((t = 6, 24, 30, 48 \text{ h})\) (fig. 8.18, 8.19). The plot (fig. 8.18) reveals a pulse energy dependency of the channel length \( y \) for all etching durations.

**Figure 8.18.** Channel length \( y \) increases with pulse energy \( E_p \) for different etching durations \((t = 6, 24, 30, 48 \text{ h})\), \(-y\)-direction and \( NA = 0.4 \) with precompensation of SA (irradiation depth \( d = 500 \mu\text{m}, f = 500 \text{ kHz}, c = 48 \% \text{ HF})\).

The channel length \( y \) increases with increasing pulse energy for all etching durations. A possible explanation for this is the larger modified cross section area \((z, w)\) resulting from higher pulse energies (see fig. 8.19). The larger cross section of a microchannel enables a

³The depletion of the acid concentration is not measured.
better exchange of fresh and depleted HF acid in the microchannel and, therefore, keeps the acid concentration stable. Due to more effective acid exchange, the channel is etched deeper. On average microchannels etched for \( t = 48 \) h are about \( \Delta y_{6-48h} = 740 \) \( \mu m \) longer than those etched for only \( t = 6 \) h. For both etch durations, the influence of the pulse energy on the channel length is relatively small (\( \Delta y \approx 150 \) \( \mu m \) for \( E_p = 0.46 \) - 1.2 \( \mu J \)). For etching times of 24 h and 30 h, the channel length reveals a limited growth dependency from the pulse energy. Shorter etching times result in shorter microchannels. At higher pulse energies (\( E_{p, t=24h} = 1.2 \) \( \mu J \), \( E_{p, t=36h} = 0.85 \) \( \mu J \)), the channels etched for 24 h and 36 h approach the maximum etching length, \( y_{48h} \approx 1300 \) \( \mu m \). Due to the decreasing energy dependency towards longer etching times, it is assumed that an etching time slightly higher than \( t = 48 \) h might result in a complete independence from the pulse energy. The low dependency between channel length \( y \) and pulse energy at low etching durations (\( t = 6 \) h) points to a too short etching duration. The cross section dimensions \( z \) and \( w \) increase with increasing pulse energy and should result in a better exchange in fresh and depleted acid. Which again should result in longer channels unless prevented by too short etching duration. At short etching times the channel is still short enough that a good exchange of fresh and depleted acid is ensured for channels nearly independent of cross section size. Since the cross section dimensions for all etching times are very similar (see fig. 8.19), the acid exchange seems to taper off the smaller the cross section dimensions and the longer the channel. Hence, beyond etching times longer than \( t = 6 \) h, the microchannel length depends more on the cross section size and therefore on the pulse energy. However, if the etching time is long enough (\( t = 48 \) h) a maximum channel length is reached and the energy dependency becomes less visible.

\(^4\text{Marked by the longest etching time (48 h)}\)
Acid concentration:
To investigate the effect of the acid concentration \( c \) on the etching behaviour, samples irradiated with different pulse energies \( E_p \) (see table 8.6) are exposed to different acid concentrations \( (c = 10\%,\ 20\%,\ 30\%,\ 48\%) \) for a duration of \( t = 6h^5 \).

<table>
<thead>
<tr>
<th>NA [1]</th>
<th>( d ) [( \mu )m]</th>
<th>( f ) [kHz]</th>
<th>( v ) [mm/s]</th>
<th>( t ) [h]</th>
<th>( c ) [%]</th>
<th>( E_p ) [( \mu )J]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>6</td>
<td>10, 20, 30, 48</td>
<td>0.14 – 1.14</td>
</tr>
</tbody>
</table>

Table 8.6.: Process parameters for microchannels \( (c: \) concentration of HF-acid, \( t: \) etching duration)\n
Comparing the channel length of microchannels etched in different concentrations of HF-acid reveals that the best results are obtained with a concentration of \( c = 30\% \) (fig. 8.20). After 6 hours, microchannels etched with \( c = 30\% \) are, depending on the pulse energy, \( \Delta y_{30\%–48\%} = 220 – 125 \mu m \) longer than the microchannels etched in \( c = 48\% \) HF-acid.

![Graph showing the relationship between pulse energy and channel length for different acid concentrations]

\[ \Delta y_{30\%–48\%} \approx 220 \mu m \]

\[ \Delta y_{30\%–48\%} \approx 125 \mu m \]

Figure 8.20.: Channel length \( y \) decreases with increasing pulse energy \( E_p \) for different HF-acid concentrations \( (c = 10, 20, 30, 48\%) \), \( \gamma \)-direction and \( NA = 0.6 \) with precompensation of SA (irradiation depth \( d = 500 \mu m \), \( f = 500 \) kHz, \( t = 6 \) h).

Accordingly, with a 30\% aqueous solution of HF-acid the microchannels are etched up to one third faster than with \( c = 48\% \). Using \( c = 30\% \) HF-acid would reduce the etching time for microchannels with the same length \( y \) by one third.

Prior to this experiment, 48\% aqueous solution of HF-acid was always used for etching since it was assumed that the Aluminum is reacting with the Fluoride [97] in the acid as follows:

\[ Al_2O_3 + 6HF = 2AlF_3 + 3H_2O \]

and then forming water soluble products

\[ AlF_3 + 3HF = H_3AlF_6 \]

\( ^5 \)6h are chosen since the dependency of the channel length \( y \) on the pulse energy \( E_p \) was minimal.

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Accordingly, it is understood that a higher concentration of Fluoride results in a faster reaction and thereby results in a reduced etching duration $t$. Further investigations are required to fully understand the mechanism of selective etching of sapphire and explain the better functionality of a 30% aqueous solution over a 48% aqueous solution of HF acid.

For $NA = 0.6$, it is observed that the channel length $y$ decreases with increasing pulse energy (fig. 8.20). This is the opposite behaviour to microchannels irradiated with $NA = 0.4$ (compare fig. 8.18). The decrease/increase for $t = 6$ h is small ($\Delta y \approx 100 \mu m$) compared to longer etching durations. Comparing the cross section length $z$ and width $w$ of the microchannels etched in different acid concentrations $c$ for both NAs reveals no large difference in cross section dimensions (see fig. 8.21). For both NAs, the cross section length $z$ and width $w$ increase with pulse energy $E_p$ (compare fig. 8.19, 8.21). This finding is not surprising since the cross section dimensions depend on the modified area. The modified volume is removed by the acid. With increasing pulse energy, and therefore increasing intensity, the cross section of the modified volume increases as well. The concentration of the acid should have no influence on the cross section dimensions $z, w$. More investigations are required to understand the difference in dependency of the channel length $y$ from the pulse energy $E_p$ for different NAs.

**Conclusion:**

Resulting from this experiments it is concluded that an etching duration of $t = 48$ h and a concentration of 30% aqueous solution of HF acid are the most suitable parameters to achieve long microchannels and repeatable results. At 48 h etching duration the channel length is only slightly pulse energy dependent.

The acid concentration $c = 30\%$ is not used for 21/2D geometries since this experiment was conducted only at the end of this work.
8.1.4. Crystalline Structure of Sapphire

The crystalline structure of sapphire changes when irradiated with tightly focused femtosecond laser radiation. This is well investigated when using laser radiation with a wavelength $\lambda = 800 \text{ nm}$, pulse duration $\tau = 200 \text{ fs}$ and focusing with high numerical aperture NA = 1.35 [12, 94, 97, 88, 113]. These investigations mainly focused on single pulse irradiation and a few investigations with multi pulse irradiation at low repetition rates ($f = 1 \text{ Hz}$). These investigations revealed that multiple irradiations of the same location result in recrystallization and therefore reduced/no selective etching of sapphire [12]. In this work, different laser ($\lambda = 1045 \text{ nm, } \tau = 500 \text{ fs}$) and focusing parameters (NA = 0.3 – 0.6) are used. Due to the high repetition rates of $f = 500 \text{ kHz}$ and moderate scanning velocities $v = 1 – 100 \text{ mm/s}$, the irradiation results in a spacial pulse overlap$^6$ of 99.8% – 81.8% (NA = 0.6) or 99.9% – 88% (NA = 0.3). Together, the parameters are significantly different from what is investigated by other groups. It is therefore expected that the results of the investigation also differ from the above mentioned results. In this work, no systematic investigation of the change in crystallinity based on the laser parameter is conducted since this would significantly change the scope of the work to develop a manufacturing process for 3D geometries in sapphire. Nevertheless, the crystalline structure and changes in the composition of the modified sapphire (NA = 0.3, pulse overlap $\approx 99\%$) areas is investigated using Raman spectroscopy and EDX measurements.

Raman spectroscopy:
Raman spectroscopy (RS) is used on a cross section cut of a modified but not etched sapphire sample. The plane of interest is the a-plane (11$\bar{2}$0) parallel to the c-axis [0001] (compare fig. 3.1). As sapphire reference an unmodified area of the same cross section is investigated (fig. 8.22). The Raman spectrum of the reference measurement shows seven active phonon modes for sapphire:

2 $A_{1g}$: 418.3 and 645.8 cm$^{-1}$
5 $E_g$: 379.9, 430.3, 449.5, 577.4, 645.8 and 751.5 cm$^{-1}$

These modes were also identified also by other groups [113, 114, 115, 116, 117] with small differences in the Raman shift mainly originating from slightly different orientation of the crystal in the experimental set-up. Du et al. assign the 645 cm$^{-1}$ and the 750 cm$^{-1}$ modes to the stretching vibration of the $[\text{Al}_2\text{O}_3]$ group [114].

The Raman spectrum of the irradiated area reveals three of the seven phonon modes (379.9, 418.3 and 751.5 cm$^{-1}$). Amorphous sapphire ($\gamma - \text{Al}_2\text{O}_3$) would not reveal any peaks in the Raman spectrum [118]. Therefore, it is presumed that the irradiated area contains amorphous sapphire as well as crystalline sapphire ($\alpha - \text{Al}_2\text{O}_3$). This assumption is supported by the nanoplanes which become visible after etching. Nanoplanes confirm a coexistence of $\gamma$ and $\alpha - \text{Al}_2\text{O}_3$ since they consist of periodic nano structures revealing material removed by etching and material not removed by etching.

In the area right next to the irradiation (fig. 8.22 red) all seven Raman peaks are detected even though they have lower intensities compared to the Raman peaks of the reference. The reduced intensity is assigned to small defects in the atomic bond of the crystalline

---

$^6$Under the spacial overlap the overlapping portion in % of the focal spot diameter $2\omega_0$ between the first and the second pulse is understood. Later on it is also referred to as pulse off-set, which describes the distance by which the second pulse is moved along an axis in relation to the first pulse.
structure, e.g. cracks, twinning or dislocation, induced into the sapphire crystal by laser induced stress. This then results in a local reduction in phonons and therefore in less intense Raman peaks.

Moon et al investigated the tensile stress due to laser irradiation with polarization microscopy (POM) and with RS [119]. They could identify a red shift of the Raman peak from 417 cm\(^{-1}\) to 415 cm\(^{-1}\) and broadening of the Raman peak (FWHM from 3.6 cm\(^{-1}\) to 11.2 cm\(^{-1}\)) after laser irradiation as an indicator for stress. Also, they were able to show that a heat treatment (1300°C for 5 h) would lead to a partial relaxation of the laser induced strain since the Raman peak was shifted back towards 416 cm\(^{-1}\) and also became less broad (FWHM: 5.5 cm\(^{-1}\)).

In the RS (fig. 8.22), conducted in this work, no such red shift or broadening of the 417 cm\(^{-1}\) (here 418.3 cm\(^{-1}\)) peak could be found, which might be caused by the difference in irradiation and laser parameters. The smaller numerical aperture (\(NA = 0.3\) instead of \(NA = 0.9/1.3\)) used in this work results in a larger focal area. Therefore, the laser induced stress caused by the amorphization is lower and spread over a larger area. The strain assigned shift in the Raman spectrum is already small (2 cm\(^{-1}\)) for a supposedly large laser induced stress. Accordingly, for smaller laser induced stress the Raman shift might be too small to be detected.

Another possibility why the Raman shift is not detected could be that the strain, which is induced by the first laser pulse, is already partially relaxed by following laser pulses. In other words, the used high repetition rate functions as a "constant" (in comparison to single pulses) heat source. If temperatures above the brittle-to-ductile transition temperature \(T_c\) (see table 3.1 in section 3.3.1) are achieved by multiple pulse irradiation of the same area, e.g. large pulse overlap, this could, according to Moon [119], also result in a partial recrystallization of sapphire.
An investigation of the accumulated temperatures during the laser irradiation has to be performed before coming to a conclusion. Further investigations of the induced change of the crystalline structure of sapphire and the laser induced stress using TEM and POM are inevitable for a proper understanding of the findings when using high repetition rates \( f \approx 500 \text{ kHz} \), moderate focusing \( \text{NA} = 0.3 - 0.6 \) and pulse durations of \( \tau = 0.5 \text{ ps} \).

**EDX-measurement:**
The EDX-measurements are conducted on a sapphire sample irradiated with the parameters displayed in table 8.2. The irradiated sample is cut in half and the cross-section is polished. One half is etched for a duration of \( t = 24 \text{ h} \) in a aqueous solution of HF-acid \( (c = 48\%) \). The other half remained unprocessed. An EDX analysis is conducted on both halves to investigate the changes in sapphire composition as a ratio of the oxygen O and aluminum Al atoms \( O : Al \). In single crystalline sapphire \( (\alpha - Al_2O_3) \), the ratio is \( O : Al = 1.5 \). For the EDX analysis, the sample is not covered with a conductive film since the coating would affect the results. An uncoated dielectric sample will promote charging\(^7\), therefore only a few measurements can be taken on every modification. Charging refers to a local electron reduction resulting in very bright spots in the SEM image (see fig. 8.24 overview).
The displayed ratios O:Al in the images (fig. 8.23, 8.24) are averaged over two measurements, either in or outside of the irradiated area. To observe the unetched modifications

![SEM micrograph of an irradiated but not etched sapphire cross section revealing nanoplanes (a). The O : Al ratio (marked by red arrows) in the enlarged pictures (b) are averaged over both points of EDX measurement.](image)

\(^7\)Tests revealed that multiple EDX/SEM measurements in a small area will lead to extreme charging and thus distort the measurement results. Over five measurements in a 150 nm radius area the measured ratio between oxygen and aluminum \( O : Al \) increases from 1.47 to 1.64. By choosing a distance of at least 500 nm between the different measurement locations, the results are not affected by charging.
by the change in crystalline structure measured by RS. The EDX measurement of the modified (dark) and surrounding areas (bright) (fig. 8.23 b)) reveal very similar ratios $O : Al$. The ratio for the modified area $O : Al = 1.43$ is slightly lower than the ratio for the surrounding area $O : Al = 1.49$. The ratio in the surrounding area matches the theoretical ratio $O : Al = 3.2 - 1.5$ of single crystalline sapphire. The lower ratio in the modified area indicates oxygen loss. Since the sapphire is irradiated in the volume it is not likely that the oxygen loss appeared during irradiation. It is more likely that water-soluble components of the modified/amorphous sapphire were washed out during the lapping and polishing process.

Investigating the laser induced modification after etching results in a very similar SEM image (fig. 8.24). Here, secondary electron detection is also used. The EDX data reveals that in the modified (fig. 8.24 a)) and surrounding areas (fig. 8.24 a), the ratio between oxygen and aluminum is reduced. In the modification, the reduction results almost in equal amounts of oxygen and aluminum atoms ($O : Al = 1.09$) (fig. 8.24 a). But measurements in the surrounding areas reveal that etching reduces the ratio of oxygen and aluminum from 1.49 to 1.39. This observation reveals that single crystalline sapphire is indeed etchable. Only in the modified area the change of the ratio $O : Al = 1.09$ is more significant. Therefore, the modification can be considered to be selectively etchable. From the RS and the EDX measurements, it can be concluded that the crystalline structure is changed due to the laser irradiation. Even though it can not be concluded to which extend the structure (amorphous/polycrystalline/crystalline) is changed. Since nanoplanes are observed, it is very likely that the irradiated area consists out of amorphous/polycrystalline and crystalline sapphire of which only the crystalline sapphire remains after etching. Moreover, crack-like structures are seen next to the nanoplanes (fig. 8.23) which require more investigation since cracks are a sign of significant stress. Stress might limit the process window or lead to poor performance of the final device due to high surface roughness. Further, TEM investigations will help in the understanding of laser induced sapphire modification since TEM enables localized measurement of the

\*\*Ratio is measured once in the direct vicinity of the modification ($\approx 500$ nm) and once about 30 µm away from the modification.
\*\*Exceeding the yield modulus of sapphire $Y = 435$ GPa.
crystalline structure. Therefore, single crystalline, polycrystalline and amorphous areas inside the sapphire can be distinguished. TEM measurements are not performed in this thesis.

8.1.5. Defects

There are several types of defects induced in the crystalline structure of sapphire by irradiation with tightly focused femtosecond laser radiation. Besides the formation desired defects\(^\text{10}\), such as nanoplanes and voids, there are undesired defects, such as twinning, slipping and cracking. These defects all result from laser induced stress. The formation of dislocations and twins along the slip planes is well investigated for different focus and laser parameters\([120, 121]\). Furthermore, the behavior of sapphire under rapid thermal loading and during crack healing/heat treatment is widely investigated since it plays an important role in LED manufacturing \([119, 122, 123]\). Also, a wide range of theoretical approaches using computer simulation, e.g. quantum mechanical calculations and molecular dynamics simulations, are applied to predict and investigate the crack formation in sapphire \([124, 125]\).

In this work, the focus is put on the formation of cracks while irradiating with tightly focused femtosecond laser radiation at a high repetition rate. Cracks restrict the process window for the fabrication of 3D components with SLE. Defects, especially cracks, which appear during the fabrication of microchannels also appear when using this technique to fabricate 3D geometries. These cracks might lead to a reduction in surface quality in terms of increased average surface roughness \(S_a\). Moreover, cracks may decrease material hardness and, therefore decreased component durability.

In the following, the relationship between crack formation and focusing properties (NA), irradiation speed \(v\) and pulse energies \(E_p\) is investigated.

**Numerical aperture NA = 0.4:**

Inspecting the microchannel cross sections irradiated with the parameters in table 8.9) reveals that the cross section morphology consists of nanoplanes (fig. 8.25 c) blue) and cracks (fig. 8.25 b) red).

\[
\begin{array}{cccccccc}
\text{NA} & d & f & v & c & t & E_p \\
\text{[\text{\mu m}]} & \text{[kHz]} & \text{[mm/s]} & \text{[\%]} & \text{[h]} & \text{[\mu J]} \\
0.4 & 500 & 500 & 2 & 48 & 48 & 0.4 – 0.8 \\
\end{array}
\]

Table 8.7.: Process parameters for microchannels (c: concentration of HF-acid, t: etching duration)

The nanoplanes are mainly oriented parallel to the [0001] axis (fig. 8.25 a)). The cracks are aligned under different angles towards the c-axis (fig. 8.25 a)). In this work, the cracks occur mainly under three different angles (20°, 27°, 32°) and seem to function either as a seed (starting point) or as a boundary (end point) to nanoplanes (see fig. 8.25 c)). The ratio nanoplanes to cracks seems to decrease towards the bottom of the cross section

\(^{10}\)Desired defects since they occur in combination with the amorphisation of the crystal which allows the selective etch ability of sapphire.

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until only cracks are found at the very bottom. The $32^\circ$ angle matches the cleavage plane (1102) of the (1120) sapphire face [122]. Prior investigations of other groups revealed that with increasing temperature (above 1500°C) sapphire tends to crack along the cleavage planes and at other angles. This may explain the crack angles $20^\circ$ and $27^\circ$ [122].

Microchannels irradiated with different pulse energies $E_p$ (fig. 8.26) reveals that these crack angles are found for all pulse energies except when SA is precompensated. When
the SA is precompensated only one crack angle (27°) is observed for different pulse energies. Similar to the findings of Guranie et al. this might point to a more thermal stress resistant fracture plane [122]. Further investigations regarding the thermal crack behaviour and the induced temperature when using femtosecond laser radiation at high repetition rates have to be conducted to support this assumption. Explanations for the different absorption processes and a timescale when the different processes take place are already given by different groups [89, 126]. The real temperature induced into the crystal by the laser pulse has not been measured and has up to now only been calculated by using different models [88, 95].

**Numerical Aperture NA = 0.6:**
Investigating the microchannel cross sections irradiated with the parameters in table 8.8 reveals a similar morphology as found for microchannels irradiated with NA = 0.4.

<table>
<thead>
<tr>
<th>NA</th>
<th>d</th>
<th>f</th>
<th>v</th>
<th>c</th>
<th>t</th>
<th>$E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>48</td>
<td>0.32 - 0.8</td>
</tr>
</tbody>
</table>

*Table 8.8.*: Process parameters for microchannels (c: concentration of HF-acid, t: etching duration)

The microchannel reveals cracks (marked red) as well as nanoplanes (marked blue). Microchannel cross sections irradiated with precompensation of SA reveal a higher density of nanoplanes (fig. 8.27 b)). The ratio of nanoplanes and cracks is different over the cross section length. Cracks mainly occur at the top third of the microchannel and propagate at an angle of 27° towards both sides of the c-axis [0001] (red line) (fig. 8.27, 8.28). Only for a pulse energy of $E_p = 0.4 \mu$J is the crack angle found to be 22° (fig. 8.28 top). Moreover, the cracks mainly occur in the upper third of the microchannel cross section and are not found to be equally distributed throughout the whole cross section. This leads to the
Figure 8.28.: Cross section of microchannels irradiated with different pulse energies $E_p$ (NA = 0.6, $f = 500$ kHz, $v = 2$ mm/s, $d = 500$ mm) without (a) and with (b) precompensation of SA. Crack angles towards the c-axis [0001] are marked. Picture without marking is for visualization of cracks.

assumption that the laser induced stress is highest in the top third of the microchannel. Besides the better visibility of the nanoplanes (high material contrast in SEM), an almost-circular area in the middle of microchannels irradiated with higher pulse energy ($E_p = 0.72, 0.8$ μJ) and precompensation of SA is found. In the circular area, no nanoplanes or cracks are visible. This area might be re-crystallized sapphire due to multiple irradiations at high pulse energy. TEM measurements are required to determine the crystalline status and prove the hypothesis.

Irradiation speed $v$:
Microchannels irradiated with NA = 0.4 and NA = 0.6 at different scanning velocities $v = 10 - 150$ mm/s and with the following laser parameters (tab. 8.9) undergo significant changes in the cross section morphology. In figure 8.29, these changes in morphology are

<table>
<thead>
<tr>
<th>NA</th>
<th>$d$</th>
<th>f</th>
<th>c</th>
<th>t</th>
<th>$E_p$</th>
<th>$v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>500</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 8.9.: Process parameters for microchannels (c: concentration of HF-acid, t: etching duration)
illustrated over the irradiation speed $v$.
For microchannels irradiated with $NA = 0.4$, increasing scanning velocity from $v = 2 \text{ mm/s}$ to $10 \text{ mm/s}$ increases crack formation and reduces of nanoplanes (compare fig. 8.26, 8.29). Increasing scanning speed further, the ratio of cracks to nanoplanes is further increased. At $v = 40 \text{ mm/s}$, only cracks and no more nanoplanes are found. Cracks align under two different angles towards the c-axis ($20^\circ$ and $27^\circ$). Starting at an irradiation speed of $v = 20 \text{ mm/s}$, small holes are observed. These holes are often located at the intersection of nanoplanes and cracks. The size of the holes increases with increasing scanning speed. Microchannels irradiated with $NA = 0.6$ have similar crack to nanoplane ratios to $NA = 0.4$. For $NA = 0.6$, cracks are aligned, at every irradiation speed, with $27^\circ$ towards the c-axis. Cracks are no longer limited to the top of the microchannel. With increasing irradiation speed, cracks are distributed throughout the microchannel cross section.

Because more cracks are found in the cross section for both numerical apertures, it is inferred that with increasing irradiation speed, the material stress increases as well. To prove this hypothesis, measurements of the laser induced stress are required. Interestingly, holes also increase in number and size with irradiation speed. In section 8.1.1, it

\[11\] Stress in a crystal induces birefringence which can be measured using POM
was observed that channel length \( (y) \) increased with increasing irradiation speed. The increase in holes diameter with irradiation speed may explain the channel length increase with irradiation speed. The exchange of fresh and depleted acid functions better with a larger exchange area. The hole diameter \( (\approx 1 \mu m) \) is larger than the nanoplanes width \( (<500 \text{ nm}) \). This supports the hypothesis of improved acid exchange resulting in longer microchannels. Further studies have to be conducted to explain the discrete angles under which the cracks appeared throughout the whole investigation.

### 8.2. Transfer to 2\(1/2\)D Geometries

The term 2\(1/2\)D geometry is used in this work to describe every geometry which is generated by combining a series of 2D geometries, e.g. microchannels. 2D geometries also includes for instance circular or rectangular geometry irradiated in a x-y plane. By aligning 2D geometries, either along the x- or z-axis, hollow planes or cuts are generated inside the sapphire sample. In both cases, the microchannels are irradiated perpendicular to the inclining laser radiation. Therefore, the irradiation is referred to as transversal writing (fig. 8.30 a),b)).

![Figure 8.30](image)

**Figure 8.30.** Transversal writing in y-z-plane (vertical alignment) (a) and x-y-plane (horizontal alignment) (b) and longitudinal writing along z-axis (c).

In section 8.1, the general feasibility of SLE and its use for the generation of microchannels with numerical apertures \( NA = 0.4 \) and 0.6 is investigated and proven. To apply this knowledge to the generation of 2\(1/2\)D geometries, it is essential to investigate the SLE process when aligning microchannels next to each other, in a x-y plane, or above each other, in different depth \( z \) of a y-z plane. Therefore, the transversal writing is investigated in section 8.2.1.

After irradiation, the samples has to be cut or lapped and polished to create access for the acid to the irradiated structure. Lapping and polishing are time consuming processes and it is therefore desirable to replace them. Accordingly, the generation of microchannels along the direction of laser irradiation, z-axis, (longitudinal writing) (fig. 8.30 c)) is investigated in section 8.2.2. Longitudinal writing would remove the lapping and polishing steps.

In section 8.2.3, transversal and longitudinal writing are combined to irradiate a hollow cubic volume. For this experiments, the irradiation is accomplished using the positioning stage. The \( \mu \text{Scanner} \) (chapter 7) is under development and not yet fully functional. The irradiation strategy is chosen to easily transfer to the \( \mu \text{Scanner} \).
8.2.1. Transversal Writing

In this section, the generation of microchannels in horizontal and vertical alignment are investigated to determine a process window to generate hollow planes and cuts in sapphire. The investigation includes the off-set between the microchannels\(^{12}\) \((\Delta z, \Delta x)\) and the number of microchannels forming the hollow plane or cut. Moreover, the pulse energy \(E_p\) is varied to identify the limits set by stress accumulation when generating large area modifications in the volume of sapphire.

The morphology of microchannels irradiated with a numerical aperture of \(NA = 0.6\) in section 8.1.5 showed a better crack to nanoplane ratio (little cracks, lots of nanoplanes) and even hollow areas if the SA is precompensated. Therefore, the following investigations are carried out with \(NA = 0.6\).

**Horizontal Alignment:**

**Number of microchannels \(N = 6\):** The horizontal alignment of microchannels is investigated first by using the irradiation parameters displayed in table 8.10.

<table>
<thead>
<tr>
<th>NA</th>
<th>(d)</th>
<th>(f)</th>
<th>(c)</th>
<th>(t)</th>
<th>(v)</th>
<th>(E_p)</th>
<th>(\Delta x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>[(\mu m)]</td>
<td>[kHz]</td>
<td>[%]</td>
<td>[h]</td>
<td>[mm/s]</td>
<td>[(\mu J)]</td>
<td>[(\mu m)]</td>
</tr>
<tr>
<td>0.6</td>
<td>200</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>1</td>
<td>0.18, 0.37</td>
<td>0 - 0.61</td>
</tr>
</tbody>
</table>

**Table 8.10:** Process parameters for hollow planes consisting of 6 overlapping microchannels \((c: \text{concentration of HF-acid}, t: \text{etching duration})\).

Hollow planes with square cross section are irradiated using the strategy shown in figure 8.31. The microchannels are irradiated in alternating directions \((+/ - y)\) along the \(y\)-axis with an off-set \(\Delta x\).

When irradiating overlapping microchannels in the volume of sapphire, stress is induced resulting in crack formation. In this work, a part of the sample is lost due to instant crack formation at a pulse energy of \(E_p = 0.37 \, \mu J\) and an off-set \(\Delta x = 0.89 - 1.11 \, \mu m\). Lower off-sets and lower pulse energies do not result in instant cracking. Nevertheless, due to induced stress, they tend to crack very easily during the preparation of cross section cuts when lapping and polishing.

Results are summarized in figure 8.32 by plotting the pulse energy versus the off-set \(\Delta x\).

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\(^{12}\) The off-set between microchannels is an absolute size which directly translates to values which can be used with the \(\mu\)Scanner. Sometimes, instead of the off-set between microchannels or focus positions, a relative size, the spatial overlap is used. This value relates to the percentage of the focal spot diameter \((2\omega_0 = 1.11 \, \mu m)\) by which two microchannels overlap.
8.2. Transfer to 2/2D Geometries

Microchannels which could be observed by optical microscopy (OM) after etching are outlined by the black boxes. Due to recrystallization of the polishing solution, only very few of those microchannels are visible during the SEM investigation\textsuperscript{13} These microchannels are marked with a green box. The cross section of the three highly visible hollow planes

![Graph](image)

**Figure 8.32.:** Plot of pulse energy $E_p$ versus microchannel off-set $\Delta x$ indicating visibility of the hollow planes by optical microscopy (OM) and scanning electron microscopy (SEM).

irradiated with $E_p = 0.18 \mu J$ are displayed in the SEM image as well as the OM image (fig. 8.33). The OM used in Through Light mode is sensitive to laser and stress induced refractive index changes, and cracks. The SEM image, on the other hand, reveals the morphology of the hollow plane cross section and the micro crystals formed by recrystallized polishing solution. The crystals are most visible around the hollow plane irradiated with an off-set of $\Delta x = 0.83 \mu m$.

The shape of the hollow plane depends on the off-set $\Delta x$ between irradiated microchannels. For hollow planes irradiated with an off-set $\Delta x = 1.11 \mu m$, equal to the theoretical focus diameter $2\omega_0$, the shape of the microchannels is still distinguishable in the cross section cut. Interestingly, the shape of the hollow plane is not rectangular as expected (compare fig. 8.33). The upper edge and the sides are rectangular, the bottom edge is neither smooth nor rectangularly aligned with the other edges. For microchannels irradiated with $\Delta x = 0.83 \mu m$, the bottom edge forms a smooth line but is also not aligned rectangular. For a smaller off-set ($\Delta x = 0.55 \mu m$), the whole structure is mirrored on the x-axis. Since the structures are irradiated from right to left, as labeled in figure 8.33, the first modification seems to affect following material absorption of laser radiation. To explain the cross section shape, the material and structural changes induced by the femtosecond laser radiation have to be taken into account.

\textsuperscript{13}The sample was etched before lapping and polishing it. It is assumed that the slurry entered the formed microchannel and was not properly removed afterwards. The remaining slurry formed crystals, either inside or at the exit of the channel, when drying. Therefore, some of the microchannel cross sections are only partial or not at all visible using SEM.
From TEM measurements conducted by Juodkazis et al., it is understood that the single-crystalline structure of sapphire becomes amorphous in the focal volume after a single femtosecond laser pulse [12, 113]. The micro-explosion from the absorption of a very intense femtosecond laser pulse causes amorphization. A tightly focused (NA = 1.3) ultrashort (200 fs) laser pulse creates intensities of about $10^{14}$ W/cm$^2$ in a sub-$\mu$m focal area which leads almost instantaneously to an ionization of the focal volume due to multiphoton ionization. This process launches a shock wave followed by fast thermal quenching. The shock wave traveling through the material and dislocating single atoms or breaking inter-atomic bonds [97] causes the amorphization. The sapphire is shock-amorphized until the pressure created by the shock wave is equal or below the Young modulus of the crystalline sapphire ($Y \approx 435$ GPa). This effect leads to a very sharp defined boundary between shock-amorphized sapphire and crystalline sapphire. The difference between amorphous and crystalline sapphire is structural and not chemical. Amorphous sapphire is less dense and has a lower refractive index, it therefore appears brighter in TEM images. For tightly focused (NA = 1.3), ultrashort ($\tau = 200$ fs) laser radiation, even void formation is observed [88]. The expansion of the amorphous areas induces stress in the surrounding crystalline sapphire [96]. This stress field can be observed directly using TEM images or with stress-induced birefringence measurements performed with an optical microscope with crossed polarizers (POM) [96]. The stress field induced with similar laser parameters, like those used in this work, was measured to propagate for more than 1 $\mu$m into the surrounding material [96]. In TEM images, the lines indicating the stress field are sharpest close to the boundary between amorphous and crystalline sapphire. Therefore, stress is highest at this boundary.

To explain the cross section shape of the hollow planes, a simple model is established. The model is based on the refractive index change due to laser induced amorphization and stress. It also includes investigations of different groups discussed earlier. In the model, the laser modification is assumed to be elliptic with a changing refractive index profile (fig. 8.34). Also, the structural changes and the laser induced pressure translate into a

\[ n_v = n_{\text{air}} = 1. \]
refractive index profile \( n(r) \). The refractive index profile is rotation symmetric around the z-axis. The center of the focal volume \( r = 0 \), where a void is found for higher NA (NA > 0.6), coincides with the position of the rotation axis of the refractive index profile.

\[ \text{Figure 8.34:} \text{ Schematic of the cross section modification created by a tightly focused femtosecond laser pulse in sapphire and the assumed refractive index profile for a rotation symmetric modification along the x-axis.} \]

To keep the model simple, the shape of the modification is assumed to be an ellipsoid with the maximum diameter at the center. The diameter is assumed to be equal to the focus diameter \( 2\omega_0 \). This simplification does not account for the effect of the pulse energy on the size of the modification. The effect of SA or other aberrations are also not included in this model.

The refractive index \( n \) in the void \( n_v \) is equal to the refractive index in air \( n_v = n_{\text{air}} = 1 \). The refractive index of the amorphous sapphire (in the modification) \( n_a \) is smaller than the refractive index of crystalline sapphire \( n_c \) but larger than the refractive index of air \( (n_c > n_a > n_{\text{air}}) \). The degree of amorphization, e.g., dislocation and broken interatomic bonds, depends on the strength of the pressure wave, which is getting weaker with increasing distance \( r \) from the void. Therefore, the refractive index in the amorphous area is a function of the radius \( n_a(r) \). The refractive index in the stress affected crystalline sapphire surrounding the modification is denoted as \( n_{ca} \). Due to the laser induced stress field, birefringence \( \Delta n_b \) occurs. At the boundary between amorphous and crystalline sapphire, the refractive index \( n_{ca} \) is highest since the laser induced stress is largest \( n_{ca}(r) = n_c + \Delta n_b(r) \). The stress induced birefringence \( \Delta n_b(r) \) decreases with increasing distance \( r \) from the focal volume until at a distance \( x \Delta n_b(x) = 0 \) and the refractive index \( n_{ca}(x) \) equals \( n_c \).

Since, it is assumed that this refractive index profile is created by the absorption of a focused femtosecond laser pulse therefore the irradiating a microchannel should also produce such profile. If the second microchannel is irradiated with an off-set \( \Delta x < x \) next to the first microchannel, the focused laser radiation is influenced by the refractive index profile of the first modification. Depending on the off-set, either only the increased refractive index of the surrounding crystalline sapphire \( n_{ca}(r) \) (for off-set \( \Delta x \geq 2\omega_0 \)) or the reduced refractive index of the amorphous sapphire \( n_a(r) \) (for off-sets \( \Delta x < 2\omega_0 \)) affect
the laser radiation of the second modification.
A higher refractive index \((n > n_c)\) leads, according to Snell’s law, to a refraction of the laser radiation in a larger angle towards the interface normal than the incoming angle. A lower refractive index \((n < n_c)\), refracts the beam in a smaller angle towards the interface normal than the incoming beam. Following, a higher refractive index results in stronger focusing and a lower refractive index results in less focusing or even defocusing. Since different rays of the laser beam during the second modification are affected by different refractive indices, this results in a distortion of the laser beam. To exactly predict the resulting focus shape, complex ray tracing would be required. Here only a simple schematic (fig. 8.35) is used trying to visualize the effect of the refractive index profile of the first modification (1) on the deformation of the laser beam during the irradiation of the second microchannel.

![Diagram](image)

**Figure 8.35.:** Schematic of the irradiation of overlapping modifications: (a) Laser focus and modification during the irradiation of the first microchannel and the second modification (b) with an off-set \(\Delta x = 2\omega_0\) or (c) \(\Delta x = \omega_0\).

During the irradiation of the second microchannel (2), with an off-set \(\Delta x \geq 2\omega_0\), the laser beam is focused in an area with stress increased refractive index \(n_{ea}\) (fig. 8.35b)). Therefore, the laser beam is focused even further. As a result, the Rayleigh length \(z_R\) is decreased and the modification is less extended in z-direction (fig. 8.35 b)).

With an offset of 0.83 \(\mu m\), as it is used in fig. 8.33, the laser beam during the second modification is affected by an increased refractive index \((n_{ea}(r))\) as well as by a reduced refractive index \(n_a\). An off-set of \(\Delta x = 0.83\ \mu m\) equals 75\% of the focus diameter \(2\omega_0\), which is assumed to also be the diameter of the first modification (1) with the refractive index \(n_a\). Therefore, 25\% of the laser beam during the irradiation of the second modification (2) is affected by the reduced refractive index of the amorphous sapphire \(n_a\) and 75\% of the laser beam is affected by the increased refractive index \(n_{ea}\) due to the stress field. The low refractive index \(n_a\) results in defocusing and the higher refractive index \(n_{ea}\) results in stronger focusing of the laser beam. Since the majority (75\%) of the laser beam is stronger focused and only 25\% is defocused, the resulting second modification (2) does not extend along the z-axis as much as the first modification (1). The hollow plane irradiated with an off-set \(\Delta x = 0.83\ \mu m\) has a similar shape as the hollow plane with the off-set \(\Delta x = 1.11\ \mu m\) (compare fig. 8.33).

For modifications irradiated with an even smaller off-set \(\Delta x = 0.5\ \mu m\) (55\% of the laser
beam diameter \(2\omega_0\), a fraction (55\%) of the laser beam is defocused due to a lower refractive index \(n_a\) in the modified area. The other 45\% of the laser beam, due to stronger focusing (\(n_b\)), still results in a modification. Both effects deform the laser beam (schematically displayed in figure 8.35c) and result in a differently shaped second modification. Accordingly, the complete shape of the hollow plane is changed when irradiating with an off-set of \(\Delta x \leq 2\omega_0\) (here \(\Delta x = 0.5 \, \mu m\)), due to the ratio of defocusing and stronger focusing.

To verify the developed model, two different irradiation methods are investigated (see fig. 8.36). In method 2, microchannels are irradiated symmetrical around the first microchannel in the centre. The irradiation direction alters from \(-y\) to \(+y\) directions resulting in microchannels irradiated in \(+y\) direction on the right side and microchannels irradiated in \(-y\) direction on the left side of the first modification. The expected cross section shape of the hollow plane is depicted in figure 8.36b) and may change with the off-set \(\Delta x\) between microchannels. The longest \(z\)-extension is expected in the center, where the first modification occurs. The shape should be relatively symmetric around the center since the stress field is expected to be more symmetrically distributed than in irradiation method 1.

In method 3, microchannels are irradiated from the outside to the inside. The two outermost channels are irradiated first and the last channel is in the centre of the stress field. Again, the irradiation direction is alternating from \(-y\) to \(+y\) direction. For this irradiation method, the longest channel extension in \(z\)-direction is expected on the right and left side of the hollow plane. The shortest extension of the microchannel cross section is expected in the center. This results in the cross section shape displayed in figure 8.36b). For irradiation methods 2 and 3, three different pulse energies \(E_p = 0.14, 0.18, 0.21 \, \mu J\) and three different off-sets \(\Delta x = 0.55, 0.66, 0.77 \, \mu m\) are investigated. A table with all resulting cross sections can be found in the Appendix A.12. For method 2 and 3, one cross section polish with the irradiation parameters \(E_p = 0.21 \, \mu J\) and \(\Delta x = 0.55 \, \mu m\) is shown in figure 8.37. The shape of the cross section does not exactly resemble the expected shape presented in figure 8.36b).

The first modification results, as predicted, in the longest extension in \(z\) direction (fig. 8.37). The rest of the cross section shape does not exactly match the prediction. Among these cross section shapes close to the prediction can be found. The miss match between real and predicted shape is assumed to be cause by crack formation in \(z\)-direction at the

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**Figure 8.36.** Schematic of irradiation strategy using method 2 and method 3 (a) for the fabrication of hollow planes with a (b) predicted cross section.
location of the first modification. Cracks, similarly to a stress field, influence the laser focus shape and the modification.

Not expected is the step like shift in the cross section of the hollow plane irradiated with method 2 (fig. 8.37). So far, a difference in channel length \( y \) and/or \( z \)-position has been observed only between single microchannels, irradiated with the same laser and irradiation parameter, but in opposite \( y \)-directions (see section 8.1.1). The irradiation direction dependency of the microchannel length \( y \) and position \( z \) is assigned to the pulse front tilt by Kazansky et al.[112]. The irradiation direction of the microchannels is indicated above the hollow plane in figure 8.37.

Moreover, the difference between real cross section shape and predicted cross section shape reveals that a more inclusive and well calculated model is required to predict the shape of the hollow plane more precisely. To build such a model, the absorbed laser energy and the change in absorption in relation to the off-set should be measured. The resulting refractive index profile and the pulse front tilt have to be measured and implemented in the model as well. From the results in this work and of other groups, it is expected that the model should also integrate used NA and pulse energy since those parameters also influence the shape and size of the modified material.

**Number of microchannels \( N > 6 \):**

The irradiation of hollow planes with rectangular cross section consisting of \( N = 40 \) microchannels is also tested by using the same laser and focusing parameters and irradiation method 3\(^{15}\) (see fig. 8.36). The hollow plane does not reveal the expected rectangular cross section shape but a mix of porous and hollow structures instead (fig. 8.38). Depending on the pulse energy \( E_p \) and the off-set \( \Delta x \) the cross section shape of the hollow plane differs (compare Appendix A.19 for an overview). All cross section cuts have in common that hollow structures appear first on the left side where microchannels are irradiated in \(+y\) direction. Irradiation in \(-y\) direction results in a porous structure (fig. 8.38). Moreover, hollow area in the cross section are more likely when irradiated with high pulse energy (\( E_p = 0.18 \ \mu J \)) and an off-set (\( \Delta x = 0.55 - 0.77 \ \mu m \)) or with smaller pulse energy (\( E_p \geq 0.15 \ \mu J \)) and smaller off-set (\( \Delta x = 0.55 \ \mu m \)). The combination of high pulse energy and low off-set results in increased crack formation.

\(^{15}\)Irradiation from the outside to the inside
Figure 8.38.: Cross section of hollow plane consisting of 40 microchannels irradiated with $E_p = 0.17 \, \mu J$ and $\Delta x = 0.66 \, \mu m$ using irradiation method 3 ($f = 500 \, kHz$, $NA = 0.6$, $v = 1 mm/s$).

In the cross section example (fig. 8.38), there are cracks at the top and bottom of the modified area. The cracks at the top are very well visible and emerge at a $45^\circ$ angle towards the inclining laser beam/the c-axis of the crystal. At the bottom, the cracks are very fine (marked by blue arrows) and emerge in a $32^\circ$ angle. As mentioned in section 8.1.5, cracks which align in a $32^\circ$ angle towards the c-axis are oriented along the cleavage plane ($\overline{10}2$). The distribution of cracks over the modification is not even. More cracks are located on the right side where the microchannels are irradiated in -$y$ direction. This also indicates an uneven distribution of laser induced stress. The conclusion drawn from this section is, that the irradiation of hollow planes extending in x-direction, perpendicular to the crystalline c-axis, is difficult to control. Hollow planes consisting of 6 microchannels can be generated. For a controlled cross section shape, the pulse energy has to be adjusted in a way that the losses, created by the lower refractive index of the modification, are compensated. Also, the SA has to be adjusted to compensate for the stronger focusing of the higher refractive index induced by the stress field. Moreover, it is suggested to control the pulse front tilt by using only one irradiation direction or adjust the tilt to zero to avoid/minimize the effect on the microchannel shape and position. Hollow planes consisting of 40 channels are not possible to generate since too much stress is induced, resulting in increased crack formation.

Vertical Alignment:
Number of microchannels $N = 40$:
The vertical alignment of microchannels, along the z axis, is investigated by using the irradiation parameters displayed in table 8.11.

<table>
<thead>
<tr>
<th>$NA$ [1]</th>
<th>$f$ [kHz]</th>
<th>$c$ [%]</th>
<th>$t$ [h]</th>
<th>$v$ [mm/s]</th>
<th>$E_p$ [$\mu J$]</th>
<th>$\Delta z$ [$\mu m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>1</td>
<td>0.15-0.36</td>
<td>2.5-3.5</td>
</tr>
</tbody>
</table>

Table 8.11.: Process parameters for cut consisting of 40 overlapping microchannels ($c$: concentration of HF-acid, $t$: etching duration)

During transversal writing with vertical alignment the microchannels are aligned on top
of each other starting with the lowest channel according to figure 8.39. The channels are irradiated in y-direction separated by an z-axis off-set $\Delta z$ and thereby form a modification in the y-z-plane.

The disadvantage of the vertical alignment is that as the irradiation depth $z$ varies, so does the SA. The manual adjustment of the correction collar at every depth is extremely time-consuming. As shown in section 8.1.2, it is also not necessary. Therefore, the SA is precompensated for the first modification at a depth $d = 200 \mu m$. It is further expected that the laser focus is less affected by the previous modification than in horizontal alignment, since the irradiation depth is always moved toward non-irradiated material.

Using the above mentioned parameters, it is possible to generate a cut extended in z-direction (compare Appendix fig. (A.20, A.21, A.22)). For low pulse energies ($E_p = 0.15 - 0.21 \mu J$), the cut is not completely hollow. Starting at $E_p \geq 0.24 \mu J$, the cut is hollow. Also, it is observed that with increasing pulse energies, the cut width $w$ increases as well. A large cut irradiated with the parameter $E_p = 0.36 \mu J$ and $\Delta z = 3.5 \mu m$, is shown

![Figure 8.39: Cross section of cut consisting of 40 microchannels irradiated in vertical alignment with a $E_p = 0.36 \mu J$ and $\Delta z = 3.5 \mu m$.](image)

in figure 8.39. The enlargement of the marked area reveals that the maximum surface roughness of the cut is $R_{max} < 1 \mu m$. This average value is also found when investigating other cuts.

The cross section length $z$ of the cut, generated in vertical alignment, varies even though they all consist of 40 microchannels (fig. 8.40). Cuts irradiated with an off-set $\Delta z = 3.5 \mu m$ are longest by about $z = 134 \mu m$. Cuts irradiated with an off-set $\Delta z = 3 \mu m$ reach a maximum length of about $z = 117 \mu m$. The shortest cuts, about $z = 98 \mu m$, are irradiated with an off-set $\Delta z = 2.5 \mu m$.

In general, it can be concluded that an off-set of $\Delta z = 3.5 \mu m$ leads to the highest productivity since less microchannels are required to fabricate a cut of a certain length $z$ than with a lower off-set. Also, so far, the graphically determined maximum surface roughness $R_{max} \leq 1 \mu m$ remains in an acceptable range$^{16}$. The irradiation of microchannels in vertical alignment is used in section 8.2.3 to fabricate 2½D geometries.

\[16\] For jewels in fine mechanics surface qualities with a roughness depth $R_z = 4 \times 16 \mu m$ and a root mean square surface roughness $R_{\sigma} = 0.8 \times 3.2 \mu m$ are requested [129], [130].
8.2. Transfer to 2/2D Geometries

![Graph](image)

**Figure 8.40:** Cross section length $z$ versus pulse energy $E_p$ for cuts consisting of 40 channel irradiated in vertical alignment for three off-sets ($\Delta z = 2.5, 3, 3.5 \, \mu m$) (NA = 0.6, $f = 500 \, kHz$, $v = 1 \, mm/s$).

### 8.2.2. Longitudinal Writing

Longitudinal writing is defined as generating microchannels by moving the laser beam along the $z$-axis. Longitudinal writing is not investigated in detail since, in this work, the main purpose of this irradiation method is to create a connection between laser modified volume and the surface.

To etch an irradiated cubic volume (fig. 8.41 a)), an access path for the acid has to be created. This is accomplished by irradiating microchannels parallel to the direction of inclining laser radiation (longitudinal writing) along the $z$-axis. The cubic volume and the four connection channels are irradiated with a velocity $v = 1 \, mm/s$ and an off-set $\Delta x = 1 \, \mu m$ or $\Delta z = 2.5/3.5 \, \mu m$. Since it is shown in section 8.2.1 (horizontal alignment)

![Diagram](image)

**Figure 8.41:** Schematic of hollow cubic volume with 4 connections to the surface (a) and the irradiation strategy for the hollow volume. [127][128]

that large area irradiation results in crack formation, a small cube with the dimensions 10 \, $\mu m \times 10 \, \mu m \times 50 \, \mu m$ (length x width x hight) is irradiated using the irradiation strategy shown in figure 8.41 b). The irradiation is conducted in several layers beginning with the lowest layer. The single layers are separated by an z-axis off-set $\Delta z$. The single modifications in one layer are separated by an off-set $\Delta z$. The top side of the cube is situated 5 – 10 \, $\mu m$ below the samples surface. After completing the cube, four inlet
channels are irradiated at the corners of the cube. After 48 hours etching in 48% HF acid, the inlet channels, irradiated in longitudinal direction, are clearly visible on the surface (fig. 8.42 b). Three of four channels are completely hollow. In one channel, remaining nanoplanes are visible. Since the nanoplanes are aligned parallel to the longitudinal channel the acid still can pass through the inlet channel.

Investigating a longitudinal cross polish of one of the hollow volumes reveals a cubic hollow structure with some nanoplanes remaining on the right and left side (fig. 8.42 a). Top and bottom sides do not reveal nanoplanes since they are aligned parallel to the nanoplanes. Nanoplanes are oriented perpendicular to the polarization direction of the laser radiation (indicated in fig. 8.42 a). In the top right corner of the cube, the round shape of the

![Image of longitudinal cross section](image)

**Figure 8.42:** SEM image of longitudinal cross section of a hollow cubic volume irradiated with $E_p = 0.28 \mu J$ and $\Delta z = 3.5 \mu m$, $\Delta x = 1 \mu m$ (a) and top view of inlet channels irradiated with $E_p = 0.24 \mu J$ (b). [127][128]

The longitudinal inlet channel is well visible (marked by a blue circle). To avoid round corners the inlet channel should be irradiated more in the center of the square. However, moving the inlet channels closer together might lead to increased crack formation. Already, with the parameters used in this experiment, crack formation in the corners of the cube and in-between the inlet channels is visible.

In this section, it is shown that longitudinal writing is a useful tool to generate an access

![Schematic of irradiation strategy](image)

**Figure 8.43:** Schematic of irradiation strategy for hourglass shaped 3D component: Irradiation of mantle face (a) and of mantle face and excess material (b) results after etching in different amount of removed material.

channel for acid to reach an in-volume modification. Moreover, it is demonstrated that
small hollow volumes can be created in the sample volume. The removal of small hollow volumes becomes important when irradiating 3D components, e.g. hourglass shape (fig. 8.43), where it is not enough to irradiate only the mantle face\(^\text{17}\) (fig. 8.43 a)). If only the mantle face is irradiated the 3D component can not be removed after etching (fig. 8.43 a)). If excess material around the narrowest section of the hourglass shape is removed as well the 3D component can be removed (fig. 8.43 b)) with etching.

### 8.2.3. Scanning Strategy for 2\(\frac{1}{2}\)D Geometry

3D components in 2\(\frac{1}{2}\)D geometry are components which have the same 2D shape (x-y plane) at every layer (z-position). For their generation, the results from section 8.2.1 are used since devices in 2\(\frac{1}{2}\)D geometry are generated by 2D shapes consisting of microchannels in vertical alignment. The extension of the component in z-direction is equal to the sample thickness \(d_s = 500/1000 \, \mu m\). Therefore, the terminology "2\(\frac{1}{2}\)D geometries are cut out of the material" will be used in this section. With this strategy, cylinders and cubes with a diameter/width of 500 – 1000 \(\mu m\) are created.

**Scanning strategy for translation stage:**

The first approach to generate 2\(\frac{1}{2}\)D geometries was conducted without and prior to the \(\mu\)Scanner. In this case, the translation stage is programmed to move the sample in a way that the laser beam describes a square or a circle in the irradiation plan (fig. 8.44a)). After finishing the 2D shape, the laser focus is moved up to the next z-position (layer) with an off-set \(\Delta z\) (fig. 8.44b)). The challenge is to prevent crack formation when using the translation stage and this irradiation strategy. Since the laser beam is not switched off while changing directions in the x-y-plane (at the halting points) or while changing the irradiation depth \(z\) (at the starting point) (fig. 8.44a)), more energy is deposited in those points. To overcome this obstacle, only very low pulse energies are applied. The irradiation time is further limited by the velocity of the translation stage \((v_{max} = 2 \, mm/s)\). Therefore, this translation stage and irradiation strategy are not suitable for industrial fabrication.

For the irradiation of cubes and cylinders in a 500 \(\mu m\) thick sapphire sample, the parameters in table 8.12 are used. The SA is precompensated for the lowest point of irradiation, the bottom of the sample at a depth of \(d = 500 \, \mu m\) (top surface \(d = 0 \, \mu m\)). The experiments in section 5.1 and the irradiation of microchannels in vertical alignment (section

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\(^{17}\)Mantel face is the micro components surface which is irradiated in the sample volume.
Table 8.12.: Process parameters for 3D components (c: concentration of HF-acid, t: etching duration)

<table>
<thead>
<tr>
<th>NA</th>
<th>f</th>
<th>c</th>
<th>t</th>
<th>v</th>
<th>$E_p$</th>
<th>$\Delta z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>1</td>
<td>0.13 - 0.27</td>
<td>3.5</td>
</tr>
</tbody>
</table>

8.2.1) revealed that it is more important to precompensate SA for the irradiation of the first microchannel than for the following microchannels. The programmed irradiation path in the x-y-plane for the translation stage (fig. 8.44 a)) contains starting and halting points. The starting/halting points are indicated, since it is expected that crack formation is most likely in areas where more laser energy is induced into the material. At a holding point (grey circle), the translation stage stops the constant movement of $v = 1 \text{ mm/s}$ to change direction. The 2D geometry is irradiated, starting and ending at the starting point (black circle). Afterwards, the position of the laser focus is moved in z-direction with the offset $\Delta z$ to a new irradiation plane, where the 2D geometry is irradiated again. This procedure is repeated until the sample is irradiated from bottom to top (fig. 8.44 b)). The first results of the irradiation strategy test for 3D component in 2½2D geometry are presented in figure 8.45.

![Figure 8.45: Overview of generated cubes. The process window ranges from $E_p = 0.2 \cdot 0.27 \mu\text{J}$. The surface roughness in the process window is $S_\alpha = 64 \text{ nm}$ and starts increasing for larger pulse energies $E_p > 0.27 \mu\text{m}$. [127]](image)

For pulse energies above $E_p > 0.2 \mu\text{J}$, the irradiated component can be removed from the sample after etching, resulting in a cube/cylinder. Below $0.2 \mu\text{J}$, the devices can not be removed from the sample because either the irradiation/modification was insufficient (fig. 8.45 left) or the kerf width is so narrow ($< 1 \mu\text{m}$) that the device gets stuck while trying to remove it from the sample (fig. 8.45 left). Above $E_p > 0.27 \mu\text{J}$, cracks start to appear along the cut direction (fig. 8.45 right) and can lead to an increased surface roughness (not measured, since it only occurs locally). Between $E_p = 0.2 \mu\text{J}$ and $E_p = 0.27 \mu\text{J}$, there is only minor crack formation at the halting/starting points and no crack formation.
8.2. Transfer to 2D Geometries

along the cut direction.
The crack formation at the halting points does not negatively affect the shape or average surface roughness $S_a$ of the cube/cylinder. The $S_a$ is measured using an AFM and is found to be $S_a = 64$ nm. The surface roughness of the polished surface is measured to be $S_a = 1.43$ nm. Optical polished surfaces are considered to have an $S_a$ of $1 - 2$ nm. Highly polished gear stones used in fine mechanics (e.g. horological industry, watt-hour-meters) have an average roughness $R_a = 0.6 - 3.2 \ \mu m$ [130]. Therefore, the surface quality of the cubes and cylinder generated with SLE is sufficient for applications in fine mechanics. The criteria for optical polished surfaces can only be met with additional post processing such as polishing.
The process window is small, $E_p = 0.2 - 0.27 \ \mu J$. This range was established prior to implementing a AOM to switch the laser on and off as needed. The irradiation velocity is also low ($v = 1$ mm/s) and therefore not suitable for industrial fabrication. Irradiating a cube with edge length of 500 $\mu m^{18}$ takes about 5 minutes. In addition, 15 minutes are required to change direction and heights. In total, irradiating a cube with these dimensions takes about $T = 20$ minutes.
To improve the fabrication time, the irradiation speed has to be increased and the idle time (direction and height changes) has to be minimized. The desired irradiation time in the range of several seconds.
It is also important that the SLE process functions as well with ruby. Ruby is used for most devices in the fine mechanical industry. Ruby’s red color makes it better visible and therefore easier to handle. This is important when manipulating components in the sub-mm scale.

**Scanning strategy for the \( \mu \)Scanner:**
The \( \mu \)Scanner is built to enable a faster (up to 100 times faster, see section 7.2) but still very precise (in the 200 - 450 nm-range) irradiation of micro components. The \( \mu \)Scanner irradiation strategy for 3D components is also broken down into a layer by layer irradiation. The important difference to solely using the translation stage is that the translation stage no longer moves the sample below the laser beam. Instead, the galvonometric scanner mirrors move the laser beam over the sample. The positioning time in the x-y plane is reduced to almost zero. By adding an AOM, the laser beam is switched off during positioning to avoid an in-homogenous irradiation. For 3D components in 2$^{1/2}$D geometries, the positioning time in z-direction can also be reduced to zero by moving the sample with a constant speed $v_z$ while the scanner mirrors are moving the laser beam with $v_{xy}$ in the x-y plane. Both velocities are synchronized so that positioning in the z-axis takes the same time $t$ as the irradiation of the 2D shape in the x-y plane. For example, a circle with the circumference $U$ is irradiated in the time $t = U/v_{xy}$. In the same time, the irradiation plane is changed by $\Delta z$ with the speed $v_z$. Therefore, the the constant speed with which the irradiation layer is changed is $v_z = \Delta z/U \cdot v_{xy}$. The synchronized movement results in a helical irradiation path with the velocity $v_{xy}$ and a pitch $h = \Delta z$ (fig. 8.46).
To test the irradiation strategy, sapphire cylinders and tubes (hollow cylinders), are irradiated with a scanning velocity of $v = 10$ mm/s ($10 \times v_{\text{transl. stage}}$) and 50 mm/s ($50 \times v_{\text{transl. stage}}$). In addition, samples with a thickness of $d_s = 1$ mm are used since this is the specimen height of the thickest components in the horologic industry. A different NA is used as well. Despite that the worst results regarding microchannel length $y$

$^{18}$ @ an irradiation speed of $v = 1$ mm/s
are achieved with NA = 0.4 (see section 8.1.1), a microscope objective with a NA of 0.4 is used for these investigations. The microscope objective LD Achromplan 20x/0.4 provides a larger scan field diameter $\varnothing_s$, suitable for the generation of components with a diameter of up to 1.2 mm. Also, as it was shown in section 8.1.1, the precompensation of SA is not so critical with this NA. For all samples, the SA is precompensated for an irradiation depth of $d = 1$ mm and remains unchanged during irradiation.

In addition to sapphire, as a sample substrate, ruby is also used to verify the SLE process for chromium doped Al$_2$O$_3$ (ruby), which is due to better visibility more often used in fine mechanics industry.

Sapphire cylinder:
To investigate the fabrication potential of cylinders with higher irradiation speed while focusing with lower numerical aperture the parameters in table 8.13 are used.

<table>
<thead>
<tr>
<th>NA</th>
<th>$f$ [kHz]</th>
<th>$c$ [%]</th>
<th>$t$ [h]</th>
<th>$v$ [mm/s]</th>
<th>$E_p$ [(\mu J)]</th>
<th>$\Delta z$ [(\mu m)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>10</td>
<td>0.18 - 0.77</td>
<td>1.45 - 11.12</td>
</tr>
</tbody>
</table>

Table 8.13.: Process parameters for cylinder ($\varnothing = 1$ mm, $h = 1$ mm) ($c$: concentration of HF-acid, $t$: etching duration)

In section 8.1.5, it is described that the increase in irradiation speed $v$ for the lower numerical apertures (NA = 0.4) resulted in increased crack formation and decreased nanoplanes/ hollow structures. Therefore, only a moderate irradiation speed of $v = 10$ mm/s is used in this experiments. Moreover, generating cubes and cylinders in earlier experiments revealed that a narrow kerf widths at low pulse energies typically result in irremovable components. To increase the kerf width, two circles with a difference in radius of 0.5 \(\mu m\)\(^{19}\) are irradiated around the same centre every z-position. The diameter of the outer circle is 1mm. The off-set in z-direction is varied from $\Delta z^{20} = 1.45 \mu m - 11.12 \mu m$.

\(^{19}\)This equals 30% of the focus diameter $2\omega_0$ for NA = 0.4.

\(^{20}\)The off-set $\Delta z$ is the distance the translation stage position is changed. The focus position in the material is changed by the value $\Delta z_{sapphire} = \Delta z / n_{sapphire}$.
The results are summarized in figure 8.47. Cylinders represented by black circles could be easily removed by pushing them out of the sample with the tip of a needle. The cylinders represented by black circles surrounded by a red square got stuck and could not be removed completely from the sample. The red triangles represent cylinders which could not be removed at all from the sample. From the graph, it is clear that an off-set $\Delta z = 1.5 - 5.9 \text{ \mu m}$ and pulse energies above $E_p = 0.33 \text{ \mu J}$ are best for the generation of removable cylinders with an irradiation speed of $v = 10 \text{ mm/s}$ (marked by black box). For larger vertical off-set $\Delta z$, a larger pulse energy might be required for the generation of cylinders. But it is also possible that the off-set $\Delta z$ is too large to ensure continuous modification.

Depending on the off-set $\Delta z$ the cylinders irradiation time $T$ ($\varnothing = 1 \text{ mm}, h = 1 \text{ mm}$) varies. The largest possible off-set $\Delta z = 5.94 \text{ \mu m}$ results in the shortest irradiation time $T = 60.3 \text{ s}$.

To compare the results obtained with the $\mu$Scanner and the translation stage, the irradiation time has to be broken down for a component of the same size. A cylinder measuring $\varnothing = 500 \text{ \mu m}, h = 500 \text{ \mu m}, \Delta z = 3 \text{ \mu m}$ and irradiated double would take $T/4$ to irradiated with the $\mu$Scanner. By using the $\mu$Scanner with an irradiation speed $v = 10 \text{ mm/s}$ ($10 \times v_{\text{translation stage}}$), the irradiation time $T$ for such cylinder is reduced from about 20 minutes (irradiation time of the translation stage) to 29.5 seconds. This results in an reduction of irradiation time $T$ by a factor of 40. Using the $\mu$Scanner has not only the advantage of higher possible irradiation speed, but also reduces the time at the halting points during direction changes to zero.

To investigate the laser induced stress, the irradiated cylinders are investigated by using polarization optical microscopy (POM) prior to etching. With this inspection method, only qualitative measurements are possible since the stress value is represented by the
brightness of the image. The less stress is induce the darker the image. The POM images of cylinders irradiated with an off-set $\Delta z = 1.51 \, \mu m$ with increasing pulse energy $E_p$ are displayed in figure 8.48 a). All images show the typical isogyre and, therefore, a shamrock-like stress distribution outside the cylinder. The distribution of the shamrock, and therefore the stress, is not very symmetrical. This is believed to be from locally reduced pulse energy due to partial vignetting of the laser beam occurring within the optical path in the µScanner.

The irradiated area is seen as a black line. With increasing pulse energy next to the dark line, a thin bright line becomes more and more dominant. Micro and nano structures induced by the laser radiation, e.g. nanoplanes, also induce an optical anisotropy into the material and therefore cause additional birefringence, which is here visible as a bright line. With increasing pulse energy, the stress is increased outside but also inside the cylinder. At $E_p = 0.4 \, \mu J$ and for an off-set $\Delta z = 1.51 \, \mu m$, the first micro-cracks appear along the irradiated circle. These cracks do not affect the shape of the cylinder nor do they damage it but they lead to an increased surface roughness. In the POM images, the cracks are visible in the less homogeneous transition from dark to bright color at the rim, inside the cylinder.

In figure 8.48 b), the stress distribution is shown for $E_p = 0.58 \, \mu J$ with increasing off-set $\Delta z$. As expected when irradiating the cylinder, increasing the off-set in the $z$-direction reduces the stress. Cylinders irradiated with an off-set $\Delta z \geq 3 \, \mu m$ do not reveal any crack formation at $E_p = 0.58 \, \mu J$. In general, for those off-sets and energies below $E_p = 0.77 \, \mu J$ crack formation is not observed.

Implementing the results of the POM investigation, the process window shown in figure 8.47 can be further separated into a process window with high surface quality (no crack formation) which excludes all pulse energies $E_p \geq 0.4 \, \mu J$ for $\Delta z = 1.51 \, \mu m$. If, besides the surface quality, irradiation time is important, the process window is reduced to the cylinders irradiated with $\Delta z = 5.94 \, \mu m$ and an irradiation time of $T = 60.3 \, s$.

Further reduction of the induced stress might be achieved by only irradiating one circle per layer and not two overlapping circles as done here. To investigate laser induced stress...
and the changes in induced stress with different irradiation strategies, POM is an easily accessible tool.

**Sapphire Tubes:**

Tubes are generated in sapphire by irradiating two circles with different diameter at every layer. The outer circle is irradiated with a diameter \( \varnothing_{\text{outer}} = 800 \ \mu\text{m} \), while the inner circle is irradiated with a diameter \( \varnothing_{\text{inner}} = 100 \ \mu\text{m} \). First, the inner cylinder is irradiated from bottom to top. Then the outer cylinder is irradiated in the same manner. Both cylinders are irradiated with the same off-set \( \Delta z \). The generation of tubes in sapphire is investigated with an irradiation speed \( v = 50 \ \text{mm/s} \) for different off-sets. The parameters used for the irradiation of a 1 mm high tube are displayed in table 8.14.

<table>
<thead>
<tr>
<th>NA</th>
<th>( f ) [kHz]</th>
<th>( c ) [%]</th>
<th>( t ) [h]</th>
<th>( v ) [mm/s]</th>
<th>( E_p ) [( \mu \text{J} )]</th>
<th>( \Delta z ) [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>50</td>
<td>0.44 – 0.86</td>
<td>0.5 – 6</td>
</tr>
</tbody>
</table>

Table 8.14.: Process parameters for tubes (\( \varnothing_{\text{outer}} = 800 \ \mu\text{m}, \varnothing_{\text{inner}} = 100 \ \mu\text{m} \) and \( h = 1 \ \text{mm} \))

\( c \): concentration of HF-acid, \( t \): etching duration

The results are shown in fig. 8.49. Tubes which can be removed from the sample after etching are marked by black circles. Black circles surrounded by a red square represent tubes which got stuck while removing them. Tubes which can not be removed from the sample are marked by red triangles. The inner cylinder could not be removed from any of the tubes. To remove the tubes, a needle is used and it is assumed, that the size of the needle tip is larger than 100 \( \mu\text{m} \) (diameter of the inner cylinder). Therefore, the force is not only applied to the inner cylinder, but also to the surrounding material.

The process window for the generation of tubes is smaller than the process window for the generation of cylinders. There are two differences during the irradiation which might

![Figure 8.49: Results for the generation of tubes with \( \varnothing_{\text{outer}} = 800 \ \mu\text{m}, \varnothing_{\text{inner}} = 100 \ \mu\text{m} \) and \( h = 1 \ \text{mm} \) irradiated with different off-sets \( \Delta z \) and pulse energies \( E_p \). The process window is marked by a black box.](image-url)
cause the difference. First, the irradiation speed for the tubes is 5 times faster than the irradiation speed for the cylinders. Second, the cylinder is double irradiated\(^{21}\) which results in a slightly wider kerf width than the single irradiation. Tubes are only irradiated once.

POM images are used to reveal the laser induced stress for the different irradiation parameters. It is interesting that all tubes which could be moved or completely removed after etching reveal a similar stress field in shape and intensity (compare Appendix A.13). In figure 8.50, the POM images for two different pulse energies and off-set $\Delta z = 1.5 - 6 \, \mu m$ are compared. Irradiations with small off-set $\Delta z = 1.5 - 3 \, \mu m$ result in more laser induced stress (brighter POM image). The stress field of the inner cylinder is due to the high laser intensity in a small area, even larger than the stress field of the outer cylinder. For two configurations, at $E_p = 0.65 \, \mu J$, $\Delta z = 1.5 \, \mu m$ and at $E_p = 0.74 \, \mu J$, $\Delta z = 3 \, \mu m$, the induced stress is large enough to result in crack formation in the inner cylinder. On the other hand, it is possible to remove tubes from the sample using these off-sets and pulse energies, after etching. Tubes irradiated with lower pulse energies or larger off-sets could not be removed from the sample. Larger pulse energy results in a larger laser modified area and, thereby, in a higher stress field and larger kerf width after etching. The kerf width of single irradiated tubes is still smaller than the kerf width of double irradiated cylinders and therefore, the process window for tubes is also smaller.

**Conclusion: Irradiation in Sapphire:**

To summarize the results of the irradiation in sapphire table 8.15 is used to compare equipment and irradiation strategies for a common shape, a cylinder\(^a\). The table compares the irradiation times $T$ a cylinder\(^a\) of $\varnothing = h = 500 \, \mu m$ irradiated once with the translation stage and at two different speeds with single and double irradiation with the $\mu$Scanner.

An obvious result is that with higher irradiation speed $v$ the irradiation time $T$ decreases. Moreover, using the $\mu$Scanner leads to a reduction of the idle time at the holding points and when adjusting the $z$-position. Combined with the increased speed $v$, the irradiation time $T$ of the $\mu$Scanner decreases by a factor of 8.3 times. Even though the irradiation time is shortest when using single irradiation with the $\mu$Scanner, the largest process window is found for double irradiation.

\(^{21}\) Two circles are irradiated for every layer with a difference in radius of 0.5 $\mu m$
8.2. Transfer to 2D Geometries

<table>
<thead>
<tr>
<th></th>
<th>Translation stage single irradiation</th>
<th>μScanner double irradiation</th>
<th>μScanner single irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v [mm/s]$</td>
<td>1</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>$NA[1]$</td>
<td>0.6</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Delta z [\mu m]$</td>
<td>3</td>
<td>0.5 – 6</td>
<td>1.5 – 3</td>
</tr>
<tr>
<td>$E_p [\mu J]$</td>
<td>0.2 – 0.27</td>
<td>0.3 – 0.77</td>
<td>0.6 – 0.86</td>
</tr>
<tr>
<td>$T(\Delta z = 3 \mu m)$</td>
<td>20 min</td>
<td>29.5 s</td>
<td>2.9 s</td>
</tr>
</tbody>
</table>

Table 8.15.: Comparison of the irradiation time $T$ for successful generated cylinders* ($\varnothing = h = 500 \mu m$) achieved with different hardware (translation stage, μScanner) and different irradiation (single, double).

Ruby cylinder:
To verify the SLE process for ruby, cylinders with a diameter of $\varnothing = 700 \mu m$ are irradiated in a $d_s = 900 \mu m$ high ruby sample. For the first experiments in ruby, very similar process parameters for the generation of sapphire cylinders are chosen. They are irradiated once at $v = 10 \text{ mm/s}$ and the SA is precompensated for the lowest irradiation depth ($d = 900 \mu m$). This parameter combination is also chosen to help distinguish if the double irradiation or the irradiation velocity influences the sapphire process window. The parameters used for the generation of the ruby cylinder are presented in table 8.16.

<table>
<thead>
<tr>
<th>NA [1]</th>
<th>$f$ [$kHz$]</th>
<th>$c$ [%]</th>
<th>$t$ [h]</th>
<th>$v$ [mm/s]</th>
<th>$E_p$ [$\mu J$]</th>
<th>$\Delta z$ [$\mu m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>10</td>
<td>0.34 – 0.8</td>
<td>1.7 – 3</td>
</tr>
</tbody>
</table>

Table 8.16.: Process parameters for ruby cylinders ($h = 0.9 \text{ mm}, \varnothing = 700 \mu m$) ($c$: concentration of HF-acid, $t$: etching duration).

Unlike sapphire samples, the orientation of the c-axis in the ruby sample is unknown. The ruby samples are chosen because these are the same samples used in the horology industry for the fabrication of jewel bearings.

The results achieved with the process parameters are displayed in figure 8.51. The first test reveals that SLE is possible with ruby, even though the process windows of ruby and sapphire are different. Only cylinders irradiated with an off-set $\Delta z = 1.7 \mu m$ and pulse energies $E_p \geq 0.69 \mu J$ can be removed from the ruby sample after etching (black circle). Cylinders irradiated with a larger off-set or lower pulse energy are not removable (red triangles). It is possible that the process window can be extended towards smaller off-set $\Delta z$ and larger pulse energies. To reveal the size of the process window additional, experiments have to be conducted. But even without further investigations it is obvious that double irradiation is beneficial and leads to an increased process window.

The cylinders which are removed from the sample are investigated using SEM and OM (fig. 8.52). The cylinder reveal well defined and crack-free edges. Also the remaining hole reveals smooth, crack-free edges. Since the SA is precompensated for a depth of $d = 900 \mu m$, the surface quality, e.g. average surface roughness $S_a$, might vary over the mantel face from bottom to top. The surface roughness could not be measured since the AFM was unavailable. Instead, a SEM was used to compare the surfaces of two ruby cylinders, one generated with SLE and another commercially fabricated ring jewel.
Figure 8.51.: Results of generated ruby cylinders ($\varnothing = 0.7 \text{ mm}, h = 0.9 \text{ mm}$) irradiated with different off-sets $\Delta z$ and pulse energies $E_p$. The process window is marked by a black box.

Figure 8.52.: SEM and OM pictures of the removed ruby cylinder and the remaining hole (top). SEM image of the surface generated by SLE is compared with a SEM image of a ring jewel fabricated commercially with the standard DIN 8257 (bottom). The average surface roughness $S_a$ of the ring jewel is indicated.

(for specifications see Appendix A.14). In the SEM image of the jewel ring the common marks of a surface processed by mechanical abrasive techniques, e.g. lapping and polishing, are visible. These craters, pits and cracks are caused by locally applied pressure which is conducted onto the surface by small particles (size: nm - $\mu$m) in the lapping or polishing solution (so called slurry). The average surface roughness of this ring jewel is
$S_a = 369$ nm. The cylinder generated with SLE has a different structure, consisting of periodic structures and some cracks, both in the sub-$\mu$m range. In general, the surface of the commercially fabricated jewel ring looks rougher than the surface generated by SLE.

**Ruby Tubes:**
Generation ruby cylinders demonstrates the feasibility to fabricate simple watch jewel geometries, like cap stones (flat cylinder shape), with SLE. Therefore, the next tested geometry is a ring jewel. The ring jewel has the shape of a flat tube and is a more complex geometry than the earlier cylinder. To irradiate a ruby tube, similar parameters to those used in sapphire (compare table 8.17) are chosen. However, to increase the probability of removing the inner cylinder and to prevent crack formation, the dimensions are slightly changed from these used in sapphire. The cylinders have diameters of $\varnothing_{\text{outer}} = 800$ $\mu$m and $\varnothing_{\text{inner}} = 400$ $\mu$m. Also, a higher irradiation speed $v = 50$ mm/s is chosen to reduce the irradiation time.

<table>
<thead>
<tr>
<th>NA [1]</th>
<th>$f$ [kHz]</th>
<th>$c$ [%]</th>
<th>$t$ [h]</th>
<th>$v$ [mm/s]</th>
<th>$E_p$ [$\mu$J]</th>
<th>$\Delta z$ [$\mu$m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>50</td>
<td>0.32-0.75</td>
<td>1-3</td>
</tr>
</tbody>
</table>

Table 8.17.: Process parameters for ruby tubes ($h = 1$ mm, $\varnothing_{\text{outer}} = 800$ $\mu$m, $\varnothing_{\text{inner}} = 400$ $\mu$m, $c$: concentration of HF-acid, $t$: etching duration).

The results of the generated ruby tubes are summarized in figure 8.53. The process window for the generation of ruby tubes with $v = 50$ mm/s is larger than the process window
for ruby cylinders with \( v = 10 \text{ mm/s} \). Tubes can be generated with a pulse energy window from \( E_p = 0.44 - 0.77 \text{ \mu J} \) for an off-set \( \Delta z = 1 \text{ mm} \). With increasing off-sets, the process window shifts to larger pulse energies. With an off-set \( \Delta z = 3 \text{ \mu m} \) the generation of tubes is only possible with a pulse energy of \( E_p = 0.77 \text{ \mu J} \). The used laser system however was limited to this pulse energies, also limiting the process window in this experiments. It is likely that the process window can be extended when larger pulse energies are applied. The irradiation time \( T \) is shorter for tubes fabricated with an off-set \( \Delta z = 3 \text{ \mu m} \) (14.6 s). Below \( E_p < 0.77 \text{ \mu J} \) and \( \Delta z = 3 \text{ \mu m} \), some tubes could be moved but not removed (black circles in red squares). Different than sapphire tubes, ruby tubes reveal no crack formation around the inner cylinder. It is assumed that the induced stress is not as high when the inner cylinder has a diameter over 100 \( \text{ \mu m} \). Since the crystalline orientation of the ruby samples is unknown and the stress field is not investigated with POM, this assumption can not be tested and proven.

Microscope images of the tubes reveal that their surfaces are crack free (fig. 8.54). Investigating the "cut" edge on the top side reveals periodic structures which are known on the surface as ripples and in the volume as nanoplanes (fig. 8.54 bottom). Similar to the ruby cylinder, the surface roughness is caused by nanostructures. Micro cracks are not visible for tubes irradiated with \( v = 50 \text{ mm/s} \). Therefore, a better average surface roughness than the ring jewel \( S_a = 369 \text{ nm} \) and even the ruby cylinder can be assumed. Due to unavailability of an AFM no actual values of the \( S_a \) could be measured.

**Conclusion: Irradiation in Ruby:**

Concluding, the generation of micro components in ruby reveals that the higher irradiation speed \( (v = 50 \text{ mm/s}) \) results in a larger process window. Further, the faster scanning
speed, 50 mm/s instead of 10 mm/s, decreases the irradiation time $T$ from 14.9 to 2.9 s\textsuperscript{22}, making the process more efficient. A comparison of the results is shown in table 8.18.

<table>
<thead>
<tr>
<th>$v$[mm/s]</th>
<th>$\mu$Scanner single irradiation</th>
<th>$\mu$Scanner single irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NA[1]$</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Delta z[\mu m]$</td>
<td>1.7 – 3</td>
<td>1 – 3</td>
</tr>
<tr>
<td>$E_p[\mu J]$</td>
<td>0.34 – 0.8</td>
<td>0.32 – 0.75</td>
</tr>
<tr>
<td>$T(\Delta z = 3 \mu m)$</td>
<td>14.9 s</td>
<td>2.9 s</td>
</tr>
</tbody>
</table>

Table 8.18.: Comparison of the irradiation times $T$ for a cylinder (diameter = height = 500 \(\mu\)m) in ruby irradiated with different irradiation speeds.

With these irradiation times, the SLE process becomes suitable for industrial production. However, since this work only shows the feasibility of SLE for ruby, more investigations, e.g. surface roughness and laser induced stress, are required to fully qualify the SLE process for industrial applications.

### 8.3. Transfer to 3D Geometries

Diagonal or curved shapes have to be produced, to generate some watch stones, e.g. balance, center or flat jewels with olivated holes. These shapes add an additional level of complexity to the process chain since these watch stones are 3D components with 3D geometry.

Different than 3D components in 2\(\frac{1}{2}\)D geometry, the 3D body can not be stacked together out of the same 2D shapes. Instead, a 3D CAD model of the component is required. The 3D model is then sliced, as described in section 7.3, to create a specific 2D model for every layer in a .JOB file format. How many .JOB files are created for a defined sample thickness $d_s$ depends on the slicing parameter and is directly linked to the off-set $\Delta z$. For example, a 100 \(\mu\)m high 3D device irradiated with an off-set $\Delta z = 10 \mu$m will consist of 10 .JOB files, while irradiated with an off-set $\Delta z = 1 \mu$m requires 100 .JOB files. Increasing the number of .JOB files, drastically increases the irradiation time $T$. Each file required a couple of seconds to load $T_{load}$ and this extra processing time is added to the total irradiation time per layer $T_{layer}$. Depending on the complexity of the 2D geometry, the filling geometry\textsuperscript{23} and the irradiation speed $v$, the irradiation time is different for every layer.

The procedure is explained exemplarily for a cone with a bottom diameter $\varnothing_{bottom} = 500 \mu$m and a top diameter $\varnothing_{top} = 300 \mu$m, irradiated with $v = 40$ mm/s. The SA is precompensated for the first layer at a depth $d = 300 \mu$m (fig. 8.55 a)).

\textsuperscript{22}Irradiation time $T$ for a cylinder with the dimensions : $h = \varnothing = 500 \mu$m

\textsuperscript{23}If, for example, an hourglass (see fig. 8.43) is generated, it is not possible to only irradiate the outer geometry of the hourglass. The widest diameter defines the outer irradiation limit and the mantle face of the hourglass defines the inner most irradiation limit. The area between both limits has to be irradiated as well, to etch it afterwards away. How this area is irradiated is defined by the filling geometry.
Figure 8.55.: Schematic of the 3D model of a cone and one layer showing the 2D geometry which is irradiated in a depth z.

According to the off-set of $\Delta z = 1 \, \mu m$, the 3D component is sliced into 300 layers. Each layer’s 2D geometry is represented by one of 300 .JOB files. One .JOB file has a loading time $T_{load}$ of approximately 2 seconds.

The irradiated mantel surface of a cone is tilted towards the incident laser radiation/z-axis. To ensure that the cone can be removed from the sample after etching the kerf has to be wider than for 3D component in 2D geometry (see double irradiation in sapphire).

To achieve a wide kerf width, the 2D geometry at every layer has a ring instead of a circle geometry (fig. 8.55 b)). The width of the ring is chosen to be about $10 \, \mu m$ to create a cut kerf with about the same width. The inside of the ring is irradiated to remove the ring material by etching. Different irradiation strategies are possible. The ring can be filled with circles with a radius $r + \Delta r$ or lines with a distance $\Delta x$ (fig. 8.56). Using filling 1 with an off-set $\Delta r = 0.82 \, \mu m$ while focusing with NA = 0.6 ($2\omega_0 = 1.11 \, \mu m$) results in an average irradiation time per layer of $T_{layer}^{24} = 0.63 \, s$. The total irradiation time for the cone sums to $T_{total} = 189 \, s$. Loading the single .JOB files takes an additional 2 seconds/file which results in a total loading time $T_{loadtotal} = 600 \, s$. Together, the irradiation time is $T = T_{total} + T_{loadtotal} = 789 \, s$ (13 minutes and 9 seconds).

Concluding, complex 3D devices are feasible. The file loading increases the total irradiation time of several minutes. Moreover, generating the .JOB files adds a new step to the process (compare process chain in section 7.3). The given example is conducted for the first test irradiations of a cone and leaves much room for improvement.

$^{24}$Irradiation time averaged over the irradiation time of each layer.
and optimization.

For the irradiation of the above described cone, the following parameters (table 8.19) are used. For the filling of the ring structure method 2 is used.

<table>
<thead>
<tr>
<th>NA [1]</th>
<th>f [kHz]</th>
<th>c [%]</th>
<th>t [h]</th>
<th>v [mm/s]</th>
<th>$E_p$ [$\mu$J]</th>
<th>$\Delta z$ [$\mu$m]</th>
<th>$\Delta x$ [$\mu$m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>500</td>
<td>48</td>
<td>48</td>
<td>40</td>
<td>0.1 - 0.21</td>
<td>0.5 - 3</td>
<td>0.55, 0.82</td>
</tr>
</tbody>
</table>

Table 8.19.: Process parameters for a cone ($h = 300$ $\mu$m, $\varnothing_{top} = 300$ $\mu$m, $\varnothing_{bottom} = 500$ $\mu$m) in sapphire ($c$: concentration of HF-acid, $t$: etching duration).

The first tests revealed that the chosen parameters lead to large crack formation. Only one cone did not reveal cracks but is insufficiently irradiated (fig. 8.57). It is assumed that crack formation is caused by too high pulse energy and a too small $\Delta z$ off-set. In addition, using filling method 2 leads to double irradiation when the filling lines cross the irradiated outside/inside line of the ring. Crossing irradiation also might promote crack formation due to locally increased energy density. In OM images after etching, it is observed that the irradiation/etching results are better on the right side. This indicates that the scan field and the sample are not adjusted parallel to each other.

Since filling method 2 is not suitable for a crack free irradiation, a second test is conducted using filling method 1 and a larger off-set $\Delta z = 3 - 7$ $\mu$m at a pulse energy $E_p = 0.16$ $\mu$J. Also the misadjustment of the irradiation plane towards the sample plane is corrected. The results of OM investigation after etching are presented in figure 8.58. Cones irradiated at $E_p = 0.16$ $\mu$J and $\Delta z = 3$ $\mu$m reveal crack-formation. At a radial off-set $\Delta r = 0.5$ $\mu$m radial as well as tangential cracks form. Whereas, at a radial off-set $\Delta r = 0.8$ $\mu$m, only tangential cracks are found. By increasing the radial off-set $\Delta r$ from 0.5 to 0.8 $\mu$m, the laser induced stress and therefore the cracks are visibly reduced. The cracks are as well reduced with increasing off-set $\Delta z$. Defect free irradiations are found for $\Delta z = 7$ $\mu$m and $\Delta r = 0.5/0.8$ $\mu$m.

Even though these irradiated cones reveal a fully etched shell without cracks, the cones could not be removed. The fabrication of 3D devices with 3D geometry adds a whole new level of flexibility and fabrication possibility to the SLE process. The increasing flexibility comes with an increased number of parameters (e.g. filling method, offset $\Delta x$, $\tau$) which have to be tested to find a process window for the fabrication of 3D devices. It is expected
that more work and tests are required before finding a suitable process window for the fabrication of these complex 3D devices.
Chapter 9.

Conclusion and Outlook

In the framework of this thesis, the generation of 2D microchannels and 3D components by SLE is investigated. A process window for SLE is determined in sapphire as well as in ruby. The detailed investigation of the impact of different irradiation and focusing parameters on the crack formation promoted the development of an empiric model to explain the variation in cross section shapes for hollow planes. Moreover, the etching parameters (time $t$, concentration $c$) are optimized. Therefore the etching time in HF-acid and with that, the post processing time, can be reduced in future from $t = 12\text{-}24\text{h}$ (48%) to $t = 6\text{h}$ (30%) for a 500 $\mu$m long microchannel.

To reduce the processing time (irradiation and adjustment time of laser/sample) a scanner system with large numerical aperture (NA = 0.3 - 1) is designed and tailored to the process demands. The combination of the scanner head with a translation stage and CAD-CAM software enables the generation of 3D components in extended substrates. The scanning system, $\mu$Scanner, is designed to be suitable for fast irradiation of sub-mm components with sub-$\mu$m precision. The high speed of the scan head (100 mm/s), combined with the here developed irradiation strategy, results in a reduction of the processing time. The irradiation time of a cylinder ($\varnothing = h = 500 \mu$m) is reduced from $T = 20 \text{ min}$ with the three axis translation stage$^1$ to $T = 2.9 \text{ s}$ with the $\mu$Scanner$^2$. This is a factor of 414. This is achieved by increasing the irradiation speed by a factor of 25 and using irradiation strategies to reduce downtimes (fig. 9.1).

In addition, the combination of the $\mu$Scanner with a translation stage also allows the generation of an array of individual microcomponents on one substrate. The size of the array is limited by the travelling range of the translation stage (here 150 mm x 150 mm). This allows for individual production without increasing costs - "Individuality for Free".

The principle feasibility of the irradiation of free-form geometries is demonstrated by irradiating a cone. To achieve this, a 3D cone model is processed with the CAD-CAM software and sliced into 2D models (.JOB files) for every irradiation height and then irradiated layer by layer. By converting the 3D model into a list of 2D models, more process parameters become available. The optimization of the new parameters is only partially conducted in this work. First tests reveal that the irradiation of a 300 $\mu$m high, 300 - 500 $\mu$m wide cone with $v = 40 \text{ mm/s}$ takes about 13 minutes. 10 of the 13 minutes are required to load the .JOB files into the scanner software. Regardless of the fact that the components of the prototype $\mu$Scanner (galvanometric scanner, translation stage and computer) do not fulfill the newest technical requirements SLE reveals a large potential as a rapid manufacturing process that decreases the irradiation/manufacturing time and

$^1 v = 2 \text{ mm/s}$

$^2 v = 50 \text{ mm/s}$
costs of corundum modifications and components. Already today, the irradiation time for the above mentioned cone can be reduced to the range of 1 minute by using up to date equipment\(^3\) and the same scanning concept. The achievable irradiation times for this equipment is shown in fig. 9.1 as μScanner II.

In addition, new scanning concepts are developed at Fraunhofer Institute for Lasertechnology to optimize the usage of newly developed femtosecond laser sources with high average power of up to 1 kW and high repetition rates of up to 56 MHz. These new technologies will support a further reduction of the irradiation time. Combined with further investigation of the process window for complex 3D components, SLE thus has the potential to become a unique rapid manufacturing process for free-form components in sapphire and ruby. This will allow for example the watch industry to implement not only new shapes but technical improvements like gear stones with a miniature oil reservoir or functional surfaces which restrict the lubricant to specific locations. Cleaning and maintenance cycles of mechanical watches could be extended by the implementation of such innovations.

The equipment developed in this work and the acquired process knowledge enables an individual and fast production of 3D components in 2\(\frac{1}{2}\)D geometry. The acquired understanding of crack formation in laser induced structures forms the foundation to optimize the fabrication of free-form 3D components or integrated devices to this effect. In addition, the μScanner can be used for the fabrication of microfluidic devices and wave guiding structures in different transparent dielectrics to efficiently produce customized labs-on-a-chip upon request as well as in-volume or surface markings in/on different materials - "Complexity for Free".

\(^3\)With a digital scan head Lightning XP 10 a irradiation speed of a factor 2.3 larger than the hurry Scan 10 is possible. With a translation stage from Aerotech the sample can be moved up to 150 times faster than with the translation stage from Kugler. Newer computers with faster processors are available to reduce the loading time of the .JOB files.
Appendix A.

Appendix

A.1. Stereolithography

Stereolithography is direct laser writing processes often used for prototyping 3D components in the µm - m range. Nano-stereolithography (NLS) is a part of stereolithography. For NLS femtosecond laser radiation is tightly focused and a high precision galvanometric scanner is utilized to move the laser focus in the focal plane. By using tight focusing feature sizes in the sub-µm range can be fabricated [131, 132]. NSL is a rapid prototyping technique and involves a layer by layer polymerization process. Therefore the 3D model is sliced into 2D models which contain the data for the irradiation of each layer. One layer is solidified according to the scanning paths of the laser radiation. The next layer is generated by translating the laser focus along the z-axis using, for example, a piezoelectric stage. In this manner, the whole structure is created by integrating each new layer to the previous solidified layer. After the laser exposure, the not solidified resin is rinsed with ethanol droplets to develop the fabricated structures.

Unfortunately, the irradiated structures were found to deform under the surface tension of the developing solvent (ethanol). Shrinkage was found to be the most prominent deformation with 2 %/µm along the substrate normal direction [132]. NLS is, aside from the generation of optical memory, micro optical components and complex microstructures, also used for the formation of photonics crystals. In photonic crystals generated with two-photon polymerization (TTP), a type of NLS, shrinkage leads to a variation in the periodicity and therefore decreases the quality of the photonic crystals. Sun et al prevented the deformation due to shrinkage by adding a correction factor to the irradiation path [133].

Also, the fabrication of complex hollow 3D shapes with TPP is problematic due to thin wall thickness after single pass irradiation. If the wall thickness is too narrow, the 3D structure will collapse due to the forces and surface tension of the developing solvent. To create thicker walls, while keeping the precision equal, multiple pass irradiation with an off-set is used. In this way, a more stable shape of the complex 3D structure is traded for high throughput. For periodic structures the high throughput is maintained by using microlens arrays or spatial light modulators creating multiple foci instead of a single focus [41, 134].

Even though NLS is a well developed rapid prototyping process it is limited to low band gap materials which fulfill the requirements for TPP. Sapphire is a large band gap material (≈ 9 eV) and requires 10 photons\(^1\) to trigger the "hard" dielectric breakdown, also

\(^1\)for a laser wavelength of \(\lambda = 1045\) nm
called optical breakdown. Therefore it is not possible to use the equipment used for TPP for the generation of sapphire micro components. Since no photomasks are required, the price for the final 3D structure mainly consist of the price for the laser source, the handling system (scanner, translation system for the resin tank) and the resin itself. The price for a 3D printer with a minimum feature size of 300 μm, a minimum layer thickness of 25 μm and a maximum 3D structure size of 125 x 125 x 165 mm can be as low as U.S. $ 3,299 \textsuperscript{2} [135]. The resin can be found for a price of U.S. $ 149 – 800 per liter. Since the processed material is restricted to curable photopolymers the choices of the materials are rather limited to mainly soft materials. By combining nano-stereolithography with a pyrolysis process at 600°C three-dimensional SiCN ceramic microstructures were build by using a newly synthesized inorganic polymer photoresist. In order to minimize shrinkage of photoresist during the pyrolysis silica nanoparticles were added as a filler [136]. Even though the fabrication of SiCN ceramic microstructures with a minimum feature size of 210 nm is possible it is quite complex and the shrinkage remained rather large with 24% of the lateral dimension.

\textsuperscript{2}Form 1 from formlabs
A.2. Photolithography

Photolithography is a process used in 2D micro-fabrication to selectively remove areas of a thin film or the bulk substrate. Therefore, a prepared substrate (cleaned and flattened) (fig. A.1a) is coated with a photoresist (resin) by spin-coating or by chemical vapor deposition (CVD) (fig. A.1b). The coating is prebaked (fig. A.1c) at temperatures of \( T = 60 - 100^\circ \text{C} \) for 5 – 30 min to remove all solvents and create a stable thin film on the substrate [137]. Afterwards, the photoresist is irradiated by projecting a photomask with UV radiation through a lens (lens not shown in fig. A.1d) onto the surface. Light, mainly UV-radiation from \( \lambda = 436 \text{ nm} \) [47] down to the EUV range (\( \lambda = 13.5 \text{ nm} \)) [138], is used to transfer geometric patterns from a mask or by interference into the photoresist. The photoresist is changed chemically and physically in the irradiated area. Since monochromatic light is used for the irradiation the inclining light interferes with the reflected light on the substrate and results in interference. A wavelike effect in the sidewalls of the photoresist is caused by the interference, called standing wave effect (fig. A.2). As pattern dimensions become smaller, these ridges (size of the used wavelength, here \( \lambda = 193 \text{ nm} \)) significantly affect the quality of the feature. Subsequently, the resist is post exposure baked (fig. A.1e).

Figure A.1.: Schematic of the different photolithography fabrication steps for a 2D structure.

Figure A.2.: SEM image of periodic pattern in lithographic structures caused by the standing wave effect without post-exposure backing a). SEM image of lithography structures after post-exposure baking b) [139].

at 100°C – 130°C to remove the standing wave effect [140]. In the following step the resist is developed by rinsing in a solvent (fig. A.1f). Using positive photoresists only the
irradiated areas are removed by the solvent due to their altered chemical properties [137]. Now the remaining photoresist is post baked (not shown in fig A.1) to remove residual solvent, water and gasses. The resin is also hardened so that it will withstand the harsh environments of etching. Afterwards the substrate with the resist is etched with a liquid (wet etching) or a plasma (dry etching) chemical agent (fig. A.1g). The chemical etching removes the uncovered substrate either isotropic if wet-etching is used or anisotropic if dry-etching is used. Higher aspect ratios are achieved and undercuts are prevented with dry-etching. Often reactive-ion etching (RIE) is used as a dry etching step since high aspect ratios can be achieved with this anisotropic process. The last process step is a cleaning step in which the remaining photoresist is removed (stripping) (fig. A.1h).
A.3. Spherical Aberration

When focussing in air, light rays are focussed by a perfect lens (aspheric shape) into one focal point on the optical axis (fig.A.3 top) regardless of their distance from the optical axis.

![Diagram of spherical aberration](image)

**Figure A.3.:** With a perfect lens (top) all rays are focused to one focal point on the optical axis. With a spherical lens (bottom) the outer rays are focused more tightly then the rays which are close to the optical axis. The extension of the focus is called positive spherical aberration.

Due to manufacturing restrictions, aspheric lenses are more expensive to fabricate, real lenses mostly have spherical shape. With spherical lenses, only the rays close to the optical axis, which are within the paraxial limit, are focused to one focal point. Rays outside the paraxial limit are focused closer to the lens surface. Marginal rays and rays close to the optical axis are focused into different focal points which leads to an extension of the beam caustic (fig. A.3 bottom). This extended focus/blurred focus is called spherical aberration. If the marginal rays are focused before the rays close to the optical axis, one speaks of positive spherical aberration.

When focussing inside a material, a focused laser beam with the geometrical focus in air \( n_{\text{air}} = 1 \) at \( z \) is shifted to a position \( z_1 = \frac{n_m}{n_{\text{air}}} z \) due to refraction at the interface (fig. A.4). In addition, spherical aberration leads to an extension of the focal spot along the propagation direction of the laser radiation (\( z \)-axis) with the value \( \Delta l \). Marginal rays are focused at the position \( z_3 \) and rays close to the optical axis are focused in \( z_1 \). Therefore the focus extension is the distance between the outer most focal points \( \Delta l = |z_3 - z_1| \). Focusing in a material leads to a negative spherical aberration since the marginal rays are focused spatially later than the rays closer to the optical axis.

In standard microscope objectives, the spherical aberration is corrected for a material depth \( d = 170 \, \mu m \) and a refractive index \( n = 1.52 \). The depth and the refractive index are the values of a cover slip used for microscopy. For material with a different refractive index or different focusing depth microscope objectives with an adjustable precompensation of

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Figure A.4.: Schematic of paraxial focusing of a light beam inside a material \( n_m \) with extension of the focal point to \( \Delta l \).

The spherical aberration are available. The spherical aberration is precompensated for by turning a correction collar, which leads to a alignment change in the microscope objective lenses. The position of the correction collar has to be calculated according to the used material and irradiation depth \( d \).
A.4. Laser Parameters

The laser performance of the µJewel D-1000 from IMRA America, Inc. is listed in table A.1. The repetition rate $f$ dependent maximum output power $P$ and pulse duration $\tau$ are listed in table A.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Performance</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition Rate $f$</td>
<td>kHz</td>
<td>100 - 5000</td>
<td>see table A.2</td>
</tr>
<tr>
<td>Output Power $P$ (compressed)</td>
<td>W</td>
<td>1.25 - 1.57</td>
<td>see table A.2</td>
</tr>
<tr>
<td>Output Power $P$ (uncompressed)</td>
<td>W</td>
<td>1.64 - 2.03</td>
<td>see table A.2</td>
</tr>
<tr>
<td>Pulse Duration $\tau$ (compressed)</td>
<td>fs</td>
<td>440 - 580</td>
<td>see table A.2</td>
</tr>
<tr>
<td>Center Wavelength $\lambda$</td>
<td>nm</td>
<td>1043</td>
<td></td>
</tr>
<tr>
<td>Emission Bandwidth (FWHM)</td>
<td>nm</td>
<td>$\leq$10</td>
<td></td>
</tr>
<tr>
<td>Polarization Ratio</td>
<td>dB</td>
<td>$\geq$20</td>
<td>linear horizontal</td>
</tr>
<tr>
<td>Beam Diameter @ 50 cm</td>
<td>mm</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Beam Propagation ($M^2$)</td>
<td></td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Beam Circularity</td>
<td></td>
<td>0.93</td>
<td></td>
</tr>
</tbody>
</table>

**Table A.1.** Specifications of the µJewel D-1000

<table>
<thead>
<tr>
<th>Rep. Rate $f$ [kHz]</th>
<th>Output Power $P$ (sech$^2$)</th>
<th>Pulse Duration $\tau$ [fs]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncompressed</td>
<td>Compressed</td>
</tr>
<tr>
<td>100</td>
<td>1.64</td>
<td>1.25</td>
</tr>
<tr>
<td>150</td>
<td>1.64</td>
<td>1.25</td>
</tr>
<tr>
<td>200</td>
<td>1.69</td>
<td>1.28</td>
</tr>
<tr>
<td>250</td>
<td>1.75</td>
<td>1.31</td>
</tr>
<tr>
<td>300</td>
<td>1.77</td>
<td>1.34</td>
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<td>400</td>
<td>1.81</td>
<td>1.37</td>
</tr>
<tr>
<td>500</td>
<td>1.83</td>
<td>1.38</td>
</tr>
<tr>
<td>700</td>
<td>1.86</td>
<td>1.42</td>
</tr>
<tr>
<td>1000</td>
<td>1.91</td>
<td>1.46</td>
</tr>
<tr>
<td>1500</td>
<td>1.96</td>
<td>1.49</td>
</tr>
<tr>
<td>2000</td>
<td>1.99</td>
<td>1.52</td>
</tr>
<tr>
<td>2500</td>
<td>2.01</td>
<td>1.53</td>
</tr>
<tr>
<td>3000</td>
<td>2.03</td>
<td>1.54</td>
</tr>
<tr>
<td>4000</td>
<td>2.06</td>
<td>1.56</td>
</tr>
<tr>
<td>5000</td>
<td>2.07</td>
<td>1.57</td>
</tr>
</tbody>
</table>

**Table A.2.** Output power $P$ and pulse duration $\tau$ dependence of the adjusted repetition rate $f$ for the µJewel D-1000.
The beam profile of the \( \mu \)Jewel without Acousto-Optic-Modulator (AOM) for different repetition rates \( f \) is circular (0.93) and reveals no distortions (\( M_2 \)) (fig. A.5). Using the AOM leads to a reduction of the beam quality since the laser beam after the AOM is no longer circular (fig. A.5 bottom right).

![Beam profile of the \( \mu \)Jewel without and with AOM for different repetition rates (marked in the picture).](image)

**Figure A.5.** Beam profile of the \( \mu \)Jewel without and with AOM for different repetition rates (marked in the picture).

The beam profile of the Satsuma from Amplitude systems can not be measured without AOM since the laser has a built-in AOM. The beam profile with AOM is round and reveals no distortion (fig. A.6).

![Beam profile of the Satsuma for one repetition rate with AOM.](image)

**Figure A.6.** Beam profile of the Satsuma for one repetition rate with AOM.
A.5. Laser Scan Head Parameters

The HurryScan®II is a compact scan head from SCANLAB AG. In this work, a scan head with a 10 mm aperture is used. The two galvanometer mirrors and the electronics are packed in a housing with the dimensions displayed in fig. A.7, A.8. The laser beam enters the scanner housing via (1) and exits it through the objective (7) in direction (8). The housing is equipped with a flange (3), mounting screws (2), alignment pins (4) and a mounting bracket (5). The electric connectors (6) are located above the beam inlet. The displacement between the entering and the exiting beam is labeled with $b$ (see fig. A.8) and for a 10 mm aperture scanner head the beam displacement $b = 12.56$ mm. The specifications of the hurryScan®II are displayed in table A.3. The typical field size is calculated under the assumption of using an f-theta objective with a focal length of $f = 160$ mm and the beam is vignetted at the objective. The writing speed is measured by writing single stroke characters of 1 mm height with the above mentioned f-theta objective. The long-term drift over 8 hours is measured after a warm-up phase.

**Figure A.7.:** Dimensions of the scanner housing are given in millimeters [141].

**Figure A.8.:** Technical drawings of the scanner housing. The beam displacement $b = 12.56$ mm describes the distance $d_1$ between scanner mirror M1 and M2 (see fig. 7.4).
<table>
<thead>
<tr>
<th>Aperture</th>
<th>10 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical performance</strong></td>
<td></td>
</tr>
<tr>
<td>Typical scan angle</td>
<td>± 0.35 rad</td>
</tr>
<tr>
<td>Typical field size</td>
<td>110 x 110 mm²</td>
</tr>
<tr>
<td>Gain error</td>
<td>&lt; 5 mrad</td>
</tr>
<tr>
<td>Zero off-set</td>
<td>&lt; 5 mrad</td>
</tr>
<tr>
<td>Skew</td>
<td>&lt; 1.5 mrad</td>
</tr>
<tr>
<td>Nonlinearity</td>
<td>&lt; 3.5 mrad</td>
</tr>
<tr>
<td><strong>Dynamic Performance</strong></td>
<td></td>
</tr>
<tr>
<td>Tracking error</td>
<td>0.14 ms</td>
</tr>
<tr>
<td>Repeatability (RMS)</td>
<td>&lt; 2 μrad</td>
</tr>
<tr>
<td>Long-term drift over 8 hours</td>
<td>&lt; 0.6 mrad</td>
</tr>
<tr>
<td><strong>Step response time</strong></td>
<td></td>
</tr>
<tr>
<td>(settling to 1/1000 of full scale)</td>
<td>0.25 ms</td>
</tr>
<tr>
<td>1% of full scale</td>
<td></td>
</tr>
<tr>
<td><strong>Typical speeds</strong></td>
<td></td>
</tr>
<tr>
<td>Marking speed</td>
<td>2.5 m/s</td>
</tr>
<tr>
<td>Positioning speed</td>
<td>10 m/s</td>
</tr>
<tr>
<td>Writing speed</td>
<td></td>
</tr>
<tr>
<td>Good writing quality</td>
<td>800 cps</td>
</tr>
<tr>
<td>High writing quality</td>
<td>500 cps</td>
</tr>
<tr>
<td><strong>Weight</strong></td>
<td></td>
</tr>
<tr>
<td>(without objective)</td>
<td>3 kg</td>
</tr>
<tr>
<td><strong>Power requirements</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±(15±1.5) V DC</td>
</tr>
<tr>
<td></td>
<td>max. 3 A</td>
</tr>
<tr>
<td><strong>Input signals</strong></td>
<td></td>
</tr>
<tr>
<td>Analog version</td>
<td>alternatively:</td>
</tr>
<tr>
<td></td>
<td>± 4.8 V; ± 9.6 V;</td>
</tr>
<tr>
<td></td>
<td>± 4.8 mA; ± 9.6 mA;</td>
</tr>
<tr>
<td>Digital version</td>
<td>XY2-100 Stannard, SL2-100</td>
</tr>
<tr>
<td></td>
<td>or optical data transfer</td>
</tr>
<tr>
<td><strong>Output signals</strong></td>
<td></td>
</tr>
<tr>
<td>Analog version</td>
<td>3 status signals per axis</td>
</tr>
<tr>
<td></td>
<td>TTL level</td>
</tr>
<tr>
<td>Digital version</td>
<td>XY2-100 Standart, SL2-100</td>
</tr>
<tr>
<td></td>
<td>or optical data transfer</td>
</tr>
<tr>
<td><strong>Operating temperature</strong></td>
<td>25 °C ± 10 °C</td>
</tr>
</tbody>
</table>

Table A.3.: Specifications of the HurryScan®II
A.6. Bravais Lattice

The space lattice can be described by a large amount of different combinations of the three basic vectors $a_i$ and different angles $\alpha_i$ in-between the basic vectors with $i = 1, 2, 3$. Due to different symmetry operations the amount of possible space lattices was reduced to 14 lattices by Auguste Bravais. The 14 Bravais lattices are separated into 7 lattice systems according to their point group\(^3\) (fig. A.9).

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Parameters</th>
<th>Simple (P)</th>
<th>Volume centered (I)</th>
<th>Base centered (C)</th>
<th>Face centered (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a_1 \neq a_2 \neq a_3$&lt;br&gt;$\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$</td>
<td>![Triclinic Diagram]</td>
<td>![Triclinic Diagram]</td>
<td>![Triclinic Diagram]</td>
<td>![Triclinic Diagram]</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a_1 \neq a_2 \neq a_3$&lt;br&gt;$\alpha_{23} = \alpha_{31} = 90^\circ$&lt;br&gt;$\alpha_{12} \neq 90^\circ$</td>
<td>![Monoclinic Diagram]</td>
<td>![Monoclinic Diagram]</td>
<td>![Monoclinic Diagram]</td>
<td>![Monoclinic Diagram]</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a_1 \neq a_2 \neq a_3$&lt;br&gt;$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$</td>
<td>![Orthorhombic Diagram]</td>
<td>![Orthorhombic Diagram]</td>
<td>![Orthorhombic Diagram]</td>
<td>![Orthorhombic Diagram]</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a_1 = a_2 \neq a_3$&lt;br&gt;$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$</td>
<td>![Tetragonal Diagram]</td>
<td>![Tetragonal Diagram]</td>
<td>![Tetragonal Diagram]</td>
<td>![Tetragonal Diagram]</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a_1 = a_2 = a_3$&lt;br&gt;$\alpha_{12} = \alpha_{23} = \alpha_{31} &lt; 120^\circ$</td>
<td>![Trigonal Diagram]</td>
<td>![Trigonal Diagram]</td>
<td>![Trigonal Diagram]</td>
<td>![Trigonal Diagram]</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a_1 = a_2 = a_3$&lt;br&gt;$\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$</td>
<td>![Cubic Diagram]</td>
<td>![Cubic Diagram]</td>
<td>![Cubic Diagram]</td>
<td>![Cubic Diagram]</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a_1 = a_2 \neq a_3$&lt;br&gt;$\alpha_{12} = 120^\circ$&lt;br&gt;$\alpha_{23} = \alpha_{31} = 90^\circ$</td>
<td>![Hexagonal Diagram]</td>
<td>![Hexagonal Diagram]</td>
<td>![Hexagonal Diagram]</td>
<td>![Hexagonal Diagram]</td>
</tr>
</tbody>
</table>

**Figure A.9.:** 14 Bravais lattices in 7 lattice systems [142]

\(^3\)the point group is a group of geometric symmetries where one point is fixed
A.7. Optical Properties of Sapphire

The optical properties of sapphire are shown in fig. A.10. At $\lambda = 1045$ nm, sapphire is transmits about $T = 84\%$ of the incident radiation.

![Figure A.10.: Transmission of sapphire [143].](image1)

The wavelength dependent refractive index of sapphire is displayed in fig. A.11. The refractive index of the ordinary ray is decreasing from the UV to the IR range from $n = 1.834$ to $n = 1.586$. At $\lambda = 1045$ nm the refractive index has the value $n = 1.75554$.

![Figure A.11.: Refractive index of sapphire measured at 24°C [144].](image2)
A.8. Hardness Scales

The Mohs scale is conventionally used in mineralogy to characterize a material’s hardness. The Mohs scale was invented by the German mineralogist Friedrich Mohs in 1812. It characterizes the scratch resistance of various materials through the ability of a harder material to scratch a softer material. The scale runs from 1 to 10 and the integers values are defined by common materials. Additional benchmarks for the hardness are given by common substances like glass, finger nail and others (fig. A.12). The Mohs scale is not linear and is not a qualitative scheme to measure the hardness. The Knoop and the Vickers hardness on the other hand are measured due to a standard. Here a diamond with a defined shape is pressed into the material with a defined force for a defined duration. The hardness is then determined by the indention of the diamond shape (A.12 top left). Different materials are represented in all three scales to give an idea about the different sizes (fig. A.12).

![Hardness of minerals I: the Mohs scale](image)

**Figure A.12.:** Hardness of minerals represented in Mohs, Knoop and Vickers scale [145], [146], [147]. Top left: Indenter shapes for Knoop and Vickers standard.
A.9. Sample Irradiation

Lapping the irradiated sample is necessary in order to remove the irregular irradiated parts due to diffraction and reflection of the laser beam on the sample’s edges (fig. A.13).

\[
\alpha_1 \quad \alpha_2 \quad \Delta \quad d
\]

\[
\text{n}_{\text{air}} \quad \text{n}_{\text{Sapphire}}
\]

**Figure A.13.** Schematic of the refraction and scattering of the laser beam at the sample interface with \( n_{\text{air}} = 1, \ n_{\text{Sapphire}} = 1.76 \). [128]

This irregularly irradiated areas (x) can be calculated: The numerical aperture (NA) is given by:

\[
NA = n_{\text{air}} \cdot sin(\alpha_1). \tag{A.1}
\]

The angle \( \alpha_1 \) results from

\[
\alpha_1 = \arcsin \left( \frac{NA}{n_{\text{air}}} \right) \tag{A.2}
\]

with \( n_{\text{air}} = 1 \) and the used objective (NA = 0.6) to \( \alpha_1 = 36.9^\circ \). Using the angle \( \alpha_1 \) and Snell’s law

\[
\frac{sin(\alpha_1)}{sin(\alpha_2)} = \frac{n_{\text{sapphire}}}{n_{\text{air}}} \tag{A.3}
\]

the angle \( \alpha_2 \) of the laser beam inside the sapphire sample is calculated as

\[
\alpha_2 = \arcsin \left( sin(\alpha_1) \cdot \frac{n_{\text{air}}}{n_{\text{sapphire}}} \right) \tag{A.4}
\]
With $n_{\text{air}} = 1$, $n_{\text{sapphire}} = 1.76$ and the angle $\alpha_1 = 36.9^\circ$ the angle $\alpha_2 = 19.9^\circ$ results. Considering the depth of the structures to be at $d = 200\ \mu\text{m}$ and the angle $\alpha_2$ and using a basic tangent function the irregularly irradiated distance is determined (Equation 2.4).

$$\tan(\alpha_2) = \frac{x}{d}$$ (A.5)

$$x = \tan(\alpha_2) \cdot d$$ (A.6)

Using the value given from equation A.4 the affected area is calculated to be $x = 73\ \mu\text{m}$ thick. This area has to be removed otherwise the acid cannot reach the homogeneously irradiated volume.
A.10. Number of Laser Passes

To investigate if similar results to the ones reported by Moser et al. [102] can be achieved with tightly focused femtosecond laser radiation, microchannels are generated using the following parameter (tab. A.4):

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>24</td>
<td>0.15 − 0.9</td>
<td>1-10</td>
</tr>
<tr>
<td>0.6</td>
<td>500</td>
<td>500</td>
<td>2</td>
<td>48</td>
<td>24</td>
<td>0.15 − 0.9</td>
<td>1-10</td>
</tr>
</tbody>
</table>

Table A.4.: Process parameters for microchannel (c: concentration of HF-acid, t: etching duration)

Comparing the channel length $y$ for different pulse energies $E_p$, ±y direction and different number of passes #, no significant decrease in the standard deviation of the channel length is found for an increasing number of passes. The standard deviation is in general rather small and ranges for all plotted data, in figure A.14, between 0.8% and 3.6% of the channel length $y$. Moser et al. do not discuss the irradiation of the mi-

![Figure A.14.: Channel length $y$ versus number of passes # for ±y-direction, for different pulse energies $E_p$ (0.48, 0.64, 0.9 μJ) and NA = 0.4 with precompensation of SA. (irradiation depth $d$ = 500 μm, $f$ = 500 kHz, c = 48 % HF, t = 24 h).](image)

crochannels. Therefore it is expected that the irradiation direction was altered back (−$y$) and forth (+$y$) (since it is easier to program) instead of irradiating only in negative or positive direction. The difference in channel length $y$ between both irradiation directions is documented in the plot (fig. A.14). With increasing number of laser passes, the channel length for ±y-direction differ less. This would also result in a smaller standard deviation, if not separated after irradiation direction.

Even though the results achieved with picosecond laser radiation can not be verified for this set up, one development seems to be intriguing. For low pulse energies ($E_p = 0.48$ μJ)
multiple irradiations do no have a negative influence on the microchannel length. Therefore the modification induced in the crystalline material might not be altered by subsequent irradiations. This is astonishing since Juodkazis et al. have shown that multiple irradiation with fs laser radiation in the infrared range result in a formation of the more thermodynamically stable polycrystalline phase [12], resulting in reduced etch ability of the material.

![Graph showing channel length vs number of passes](image)

**Figure A.15.** Channel length $y$ versus number of passes $\#$ for $\pm y$-direction, for different pulse energies $E_p$ (0.18, 0.24, 0.74 $\mu$J) and NA = 0.6 with precompensation of SA. (irradiation depth $d = 500$ $\mu$m, $f = 500$ kHz, $c = 48$ % HF, $t = 24$ h).

For higher pulse energies ($E_p = 0.66, 0.9$ $\mu$J), there seems to be an optimum value of $\# = 3$ passes for the fabrication of channels. Higher numbers of passes result in a decreased channel length which might be due to the change of the amorphous to the polycrystalline phase. The change in the refractive index of the material induced by the first irradiation and the influence of the change in refractive index on the focus shape during the subsequent irradiations as well as the change of the ablation/modification threshold due to incubation effects [148, 149] might also affect the results. Further investigations are required to determine the effect of the different processes.

Interestingly enough, at higher numerical aperture (0.6), the channel length $y$ plotted versus the number of passes $\#$ reveals that the channel length increases with increasing pulse energy $E_p$ as well as with the number of passes. The growth of the curve is limited, the channel length $y$ increases fast at small number of passes and reaches a saturation at $\# = 5$ passes for low pulse energy $E_p = 0.18$ $\mu$J and at $\# = 3$ passes for higher pulse energy $E_p = 0.42 - 0.74$ $\mu$J. This result is also not in agreement with the investigation and results made by Juodkazis et al. [12]. Further investigations, especially TEM measurements, should be carried out to investigate the state of the crystalline phase after each pass.

In agreement with the measurements with multiple passes and smaller NA (0.4), no dependency of the standard deviation from the number of passes is found. The findings from Moser [102] et al. can not be supported by these experiments.
A.11. Qualitative Comparison of Different NAs

Qualitative comparison of NA = 0.3 - 0.8:

The cross section shape and structure varies with the numerical aperture of the microscope objective. So far in this work only microscope objectives with NA = 0.4/0.6, resulting in NA = 0.3/0.6 due to the laser beam diameter $\Omega = 5$ mm, are used. To investigate the influence of the NA on the cross section shape and structure addition microchannels are irradiated with a numerical aperture of NA = 0.7 and 0.8 and etched in an aqueous solution of HF-acid, $c = 48\%$, for $t = 24$ h. The microchannels are irradiated either with a pulse energy $E_{pL} = 1$ $\mu$J or 5 $\mu$J. Different from previously-described experiments, the transmission of the microscope objectives is not known for all objectives. Therefore, the pulse energy is measured only at the laser outlet $E_{pL}$ and does not resemble the pulse energy after the microscope objective at the sample $E_p$. This uncertainty will not allow a quantitative comparison of cross section length $z$ and width $w$, but it still allows a qualitative comparison of the formed structures.

Microchannels irradiated with NA = 0.3 consists only of periodical nano structures with a distance of about 400 nm (fig. A.16a). The periodic structures are also investigated by other groups and were first called nanogratings and later named nanoplanes by Hnatovsky [99, 151, 152]. It was proven that nanoplanes are ripples continuing in the volume of the sample [153] and the distance or periodicity of the nanoplanes mainly depends on the laser wavelength $\lambda$ and the irradiated material.

Using a higher NA = 0.6 results in the formation of hollow channels surrounded by nanoplanes (fig. A.16b). The hollow channels form in two areas in the top half of the structure. Different groups have investigated the damage induced in transparent materials, mainly fused silica but also sapphire and found similar damage formations, which are either denoted to filamentation [154] or to not completely compensated spherical aberration [155].

At a slightly higher NA = 0.7, but also higher laser pulse energy $E_{pL} = 5$ $\mu$J, an elongated
hollow channel is formed in the middle, framed by nano planes on the outside (fig. A.16c). The hollow structure is slightly narrower in the middle than on top and bottom. This would coincide with the formation of hollow channels starting in two areas and overlapping in the middle, as seen with NA = 0.6. Very similar cross sections of laser irradiation were found by Juodkazis using high numerical apertures (NA = 1.35), pulse durations of $\tau = 180$ fs and multiple irradiation of the same spot ($> 2$) [156]. Juodkazis assigns the effect to field enhancement after multiple laser pulses. Moreover it is shown that the refractive index is changed due to laser induced change in the material density [95]. The change in refractive index also has an effect on the focus shape of the next laser pulse.

Using a numerical aperture of NA = 0.8 results in a hollow microchannel without visible nanoplanes (fig. A.16b). The structure around the hollow part of the microchannel was disrupted during the lapping process. This is often found when using high pulse energies and also with lower numerical apertures. It seems that the surrounding area is weakened by the irradiation and therefore breaks easily during the lapping process. Gamaly and Juodkazis have shown that due to the formation of a void (hollow volume in the middle of the focus) and the structural change of the surrounding material (transformation from crystalline to a amorphous phase) stress is induced in the focus area [94, 88, 95]. The laser induced stress, in addition to the stress during the lapping, could result in a damaged structure as shown in figure A.16 d).
A.12. Hollow Plans and Cuts

Microchannels with a large size cross section (several \( \mu \text{m} \)) either in horizontal direction (hollow plan) or in vertical direction (hollow cut) are generated. For this purpose 6 – 40 adjacent microchannels are irradiated in a depth \( d = 500 \mu \text{m} \) with precompensation of SA in horizontal alignment.

A model is developed based on the expected laser induced stress to predict the cross section shape of different irradiation methods. In addition different irradiation methods tested and used for validation of the model. Figures A.17, A.18 present the resulting cross-section shapes achieved with irradiation method 2 and 3. In both cases 7 microchannels are aligned horizontally. The trial of creating hollow planes consisting of 40 microchannels,

![Figure A.17.](image) Cross section micrograph of hollow consisting of 7 microchannels irradiated using irradiation method 2 with indicated pulse energies \( E_p \) and off-sets \( \Delta x \) (NA = 0.6, \( f = 500 \text{ kHz}, v = 1 \text{ mm/s}, c = 48 \%, t = 24 \text{ h} \)).

irradiation with method 3 does not result in a hollow cross section (fig. A.19 ). It is assumed the due to too much laser induced stress the observed porous structure is created. For hollow cuts microchannels are irradiated on top of each other (vertical alignment) with an off-set \( \Delta z \). The hollow cuts in this example consist of 40 microchannels and reveal a hollow cross sections. The results of hollow cuts irradiated with an offset \( \Delta z = 2.5 \mu \text{m} \) are displayed in figure A.20. The results of vertical microchannels irradiated with an offset \( \Delta z = 3 \mu \text{m} \) are presented in figure A.21 and in figure A.22 for an offset \( \Delta z = 3.5 \mu \text{m} \).
Figure A.18.: Cross section micrograph of hollow plan consisting of 7 microchannels in horizontal alignment irradiated using irradiation method 3 with indicated pulse energies $E_p$ and off-sets $\Delta x$ (NA = 0.6, $f$ = 500 kHz, $v$ = 1 mm/s, $c$ = 48 %, $t$ = 24 h).

Figure A.19.: Cross section micrograph of hollow plan consisting of 40 microchannels in horizontal alignment irradiated using irradiation method 3 with indicated pulse energies $E_p$ and off-sets $\Delta x$. The irradiation direction is indicated in the top right corner (NA = 0.6, $f$ = 500 kHz, $v$ = 1 mm/s, $c$ = 48 %, $t$ = 24 h)
**Figure A.20.** Cross section of hollow cut consisting of 40 microchannels irradiated in vertical alignment with an off-set of $\Delta z = 2.5 \, \mu m$ and indicated pulse energies $E_p$ ($NA = 0.6$, $f = 500 \, kHz$, $v = 1 \, mm/s$, $c = 48 \, \%$, $t = 24 \, h$).

**Figure A.21.** Cross section of hollow cut consisting of 40 microchannels irradiated in vertical alignment with an off-set of $\Delta z = 3 \, \mu m$ and indicated pulse energies $E_p$ ($NA = 0.6$, $f = 500 \, kHz$, $v = 1 \, mm/s$, $c = 48 \, \%$, $t = 24 \, h$).
Figure A.22.: Cross section of hollow cut consisting of 40 microchannels irradiated in vertical alignment with an off-set of $\Delta z = 3.5 \, \mu m$ and indicated pulse energies $E_p$ ($NA = 0.6$, $f = 500$ kHz, $v = 1$ mm/s, $c = 48 \%$, $t = 24$ h).
A.13. Sapphire Tubes

Sapphire tubes with an outer diameter $\varnothing_{\text{outer}} = 800 \ \mu\text{m}$ and an inner diameter $\varnothing_{\text{inner}} = 100 \ \mu\text{m}$ are irradiated with a speed $v = 50 \ \text{mm/s}$, different pulse energies $E_p$ and off-sets $\Delta z$. The SA is precompensated for the first irradiation layer in a depth $d = 1000 \ \mu\text{m}$.

The tubes are investigated using POM before removal from the sample. With POM the laser induced stress is made visible due to the change in birefringence. The brightness of the POM images directly resembles the laser induced stress. A POM image of not irradiated sapphire in c-orientation results in a dark picture. Tubes which could not be removed from the sample after etching are marked by a red box A.23.

![Image of POM images](image.png)

**Figure A.23.:** Polarization microscope images (POM) reveal the laser induced stress of tubes irradiated with pulse energies $E_p = 0.47 - 0.86 \ \mu\text{J}$ for different offsets $\Delta z = 0.5 – 3 \ \mu\text{m}$. Tubes which are not completely removed after etching are marked by a red box, all other tubes are removed.
A.14. Standard for Watch Jewels

Ring jewels are used in fine mechanics, wrist watches as also in technical devices, such as flow meters. In figure A.24, the standard for ring jewels used in horology (watch) industry, is displayed. For devices in horology industry often no specific defined surface qualities are named. To find out about the average surface qualities, single watch stones are investigated by AFM. The average surface roughness of a ruby ring jewel is $S_a = 369$ nm.

SEM pictures of the surface are displayed in figure A.25. For devices in fine mechanics, such as a jewel with concave shape for a wattmeter, the surface roughness is specified.
Figure A.25.: SEM images of a ring jewel commercially fabricated out of ruby with the standard DIN 8257. The average surface roughness $S_a$ off the outer surface is indicated in the bottom left picture.

in standard DIN 3141 row 3. The surface quality of defined surfaces requires an average surface roughness $S_a = 0.6 \mu m - 3.2 \mu m$ (fig. A.26). The surface quality of less important surfaces is undefined or unspecific, as in the horology industry.
A.14. Standard for Watch Jewels

**Figure A.26.** DIN-standard for the fabrication of jewels with concave shape for wattmeters.

<table>
<thead>
<tr>
<th>d</th>
<th>h</th>
<th>r</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,8</td>
<td>1,2</td>
<td>0,75</td>
<td>± 0,05</td>
</tr>
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<td>± 0,03</td>
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<tr>
<td>2,6</td>
<td>1,4</td>
<td>1,1</td>
<td>± 0,05</td>
</tr>
</tbody>
</table>

Werkstoff: synthetischer Saphir, weiß (andere Werkstoffe nach Vereinbarung)

**Anforderungen an die Kalottenoberfläche**

Zur Beurteilung der Oberfläche der Hohlung ist diese in Zonen eingeteilt und zwar in eine Laufzone (untere 2/3 der Hohlungsstiefe t) und eine Randzone (oberes Drittel der Hohlungsstiefe t).

- **a.)** Laufzone (untere 2/3 der Hohlungsstiefe t): Sprünge, Kratzer, Löcher und Gasbläsen sind nicht zulässig.
- **b.)** Randzone (oberes Drittel der Hohlungsstiefe t): Sprünge, Kratzer und Löcher sind nicht zulässig; auflaufendes Bearbeitungsgewebe und tiefliegende Gasbläsen werden toleriert.

Die Prüfung der Oberflächengüte erfolgt mit einem Stereomikroskop bei 60 bis 70-facher Vergrößerung und Auflichtbeleuchtung. Die Politurstufe soll den lapidarischen Anforderungen und herstellungstechnischen Möglichkeiten entsprechen, im Kalottenzentrismus bestmöglich sein und kann gegen den Rand hin abschmelzen.

**Fachnormenausschuß Uhren im Deutschen Normenausschuß (DNA)**

Deutsche Elektrotechnische Kommission - Fachnormenausschuß Elektrotechnik im DNA gemeinsam mit Vorschriftenausschuß des VDE
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