Chapter 4

Fabrication of Micro-optics in Polymers and in UV Transparent Materials

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Abstract

Various laser-based approaches for the fabrication of micro-optical components in quartz and polymers have been studied. The fabrication of Fresnel micro-lens arrays in polymers is achieved by the combination of laser ablation and the projection of a *Diffractive Gray Tone Phase Mask* (DGTPM). Arrays of diffractive and refractive micro-lenses in quartz are fabricated by a laser assisted wet etching process and the projection of a DGTPM. An array of plano-convex micro-lenses was utilized as a beam homogenizer for high power Nd:YAG lasers.

Keywords: Diffractive Gray Tone Phase Mask (DGTPM); Excimer laser; Fresnel micro-lens; Lambert–Beer law; Laser ablation; Laser Induced Backside Wet Etching (LIBWE); Photothermal; Plano-convex micro-lenses.

4.1. Introduction

Recent developments in telecommunication and miniaturization of optoelectronic-mechanical devices stimulate the investigations of new techniques for fast micro-machining of optical elements. Arrays of micro-lenses fabricated in polymers or in quartz are the key elements in modern optics and optoelectronics [1–8]. The unique properties of micro-lenses such as small dimensions and short focal length are utilized in high precision imaging systems, e.g. copiers, printers, and fax machines. The advantages of micro-optical components fabricated in polymers compared to large scale lenses are the flexibility and easy integration into complex micro-optical systems [4,7]. Arrays of micro-lenses are widely used in telecommunication and

The most established techniques for the fabrication of micro-optical components in polymers and in plastics are hot embossing and injection molding. These techniques are commercialized and are applied for the mass production of submicron gratings and micro-lenses in polymers [4,6,14–17]. Replication technology is the key to the one step process and provides a very economical way of producing micro-optical elements in polymers. The key issues for this process are the complex master masks and the limited number of polymers that can be used. An alternative one step process for micromachining of micro-optical elements in polymers is direct exposure of polymers to a focused laser beam or a beam which is imaged through a circular aperture [2,4,7,18–22]. HeCd, ArF, KrF, or XeCl excimer [2,4,20] lasers as well MID IR CO_2 laser [13,23] can be used as irradiation sources.

An alternative one step process for the fast fabrication of complex structures with continuous profiles, e.g. Fresnel micro-lenses in polymers has been demonstrated by David *et al.* [24]. This method will be described in detail later.

UV transparent materials, e.g. quartz, BaF_2, and sapphire have much higher damage thresholds for UV laser irradiation. Therefore, micro-lenses in UV transparent materials, e.g. quartz, are applied in a number of application, such as optical connectors in telecommunication, imaging, wavefront measurements, and beam homogenizing [1,4,7,9,13,25–36].

UV transparent materials, e.g. quartz, can be directly ablated with ultrafast lasers [30,37–48], Vacuum Ultraviolet lasers (VUV) (157 nm, 11 ns) [32,49–53] or by the combination of a VUV laser with a KrF excimer laser [54–57]. MID IR lasers, e.g. CO_2 laser can also be applied for the fabrication of refractive micro-lenses, e.g. on the end of an optical fiber [9]. Another possibility is the fabrication of micro-optics in quartz by using the sequential scanning of a focused ion beam [14,57,58].

An alternative approach for the structuring of micro-optical components in solid state materials is laser assisted etching. The laser light passes through the transparent substrate and is strongly absorbed by a media which is in contact with the material. The highly absorbing media can be in the form of a gas [59], a solid material [60,61], or liquids [62–71], which will be described in detail later. The combination of laser assisted wet etching with the projection of a *Diffractive Gray Tone Phase Mask* (DGTPM) can be applied as an alternative technique for the fabrication of micro-optical components in quartz [31,72,73], which are applied as beam homogenizers for high power lasers.

In this chapter we will give a brief overview of laser ablation of polymers which is the basis for laser fabrication of micro-optical elements in polymers. The focus of this chapter will be on the application of laser ablation and Laser Induced Backside

Wet Etching (LIBWE) combined with the projection of DGTPM for the fabrication of complex three-dimensional structures, such as plano-convex and Fresnel micro-lens arrays, in polymers, and UV transparent materials.

4.2. Laser Ablation of Polymers

Laser ablation of polymers was first reported in 1982 by Srinivasan *et al.* [74] and Kawamura *et al.* [75]. The discovery of laser ablation of polymers initiated research projects around the world and is today industrially used for the production of nozzles for inkjet printers [76], to prepare the via-holes in multichip modules by IBM [77], and for the fabrication of micro-optical components [2,4,13,18,21,22,78,79].

4.2.1. Mechanisms and Models

The mechanisms of polymer ablation are typically described as photochemical, photothermal, photophysical or as a combination of those, and can be described briefly as follows:

Photochemical: Electronic excitation results in direct bond breaking [80–84].

Photothermal: The electronic excitation is thermalized on a ps timescale, resulting in thermal bond breaking [85–89].

Photophysical: Thermal and non-thermal processes play a role. In this model two independent channels of bond breaking [90,91] or different bond breaking energies for ground state and electronically excited states chromophores are applied [92,93]. This model is most adequate for short laser pulses in the ps and fs range [94].

Another method to describe the different ablation processes is a separation into surface and volume models. The volume model describes the ablation process within the bulk of the material. In the surface models, only a few monolayer of the material are considered. The different models can be described as follows:

Photochemical surface model: Valid for long pulses and higher irradiation fluences [95].

Thermal surface model: The model does not consider the sharp ablation threshold, but can describe the occurrence of an *Arrhenius* tail, which is the linear dependence of the ablation rate with the irradiation fluence at low fluences, that is observed when the ablation rate is determined with mass loss measurements [85,89,90,96].

Photochemical volume model: The model describes a sharp ablation threshold, but the Arrhenius tail is not accounted for [80–82,84,97].

Thermal volume models: These models are often oversimplified by reducing the movement of the solid–gas interface and results therefore in too high temperatures [88,98].

In newer models, several mechanisms of the listed above are combined, e.g. in the volume photothermal model of Arnold and Bityurin [99], that combines features of the photochemical and the thermal surface models. This model includes many material parameters. Several of these parameters are obtained from fitting of experimental data, and have to be adjusted to fit each polymer.

Polymers that show a photochemical ablation behavior at the irradiation wavelength are preferable for structuring, as the damage of the surrounding material due to a thermal processes is minimized. A conversion of the polymer into gaseous product is also of advantage, as no or only minor amounts of ablation products are redeposited on the structured surface, and additional cleaning procedures may not be necessary.

The ablation process is often described by an Lambert–Beer law related Equation (1) [80,100]:

$$d(F) = \frac{1}{\alpha_{\mathrm{eff}}} \ln\left(\frac{F}{F_{\mathrm{th}}}\right) \tag{1}$$

where $d(F)$ represents the ablation rate per pulse, α_{eff} is the effective absorption coefficient, F is the irradiation fluence, and F_{th} is the ablation threshold fluence.

The dependence of the ablation rate on the irradiation fluence can often not be described by a single set of parameters. In Fig. 1 an example of the dependence of the ablation rate of a polymer on the irradiation fluence is shown. Three fluence regions can be distinguished. From the low fluence range the ablation threshold fluence is defined. The threshold fluence is defined as the lowest fluence, where the onset of ablation can be observed. It is also noteworthy to mention, that in the low fluence range, ablation does not necessarily start with the first pulse, but after multiple pulses. This phenomenon is known as *incubation* and is related to a modification of the polymer by the previous laser pulses [101], which increases the absorption at the irradiation wavelength. Incubation is normally observed only for polymers with low absorption coefficients at the irradiation wavelength.

In the intermediate fluence range an increase of the slope of the ablation rate is often observed. This increase in the ablation rate may be due to an additional or more effective decomposition of the polymer by energy that has been gained from

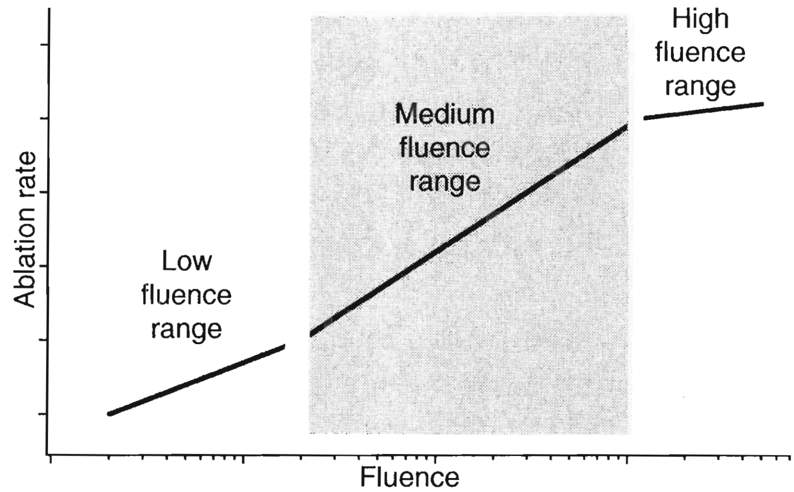


Figure 1: Schematic illustration of the fluence dependence for the ablation rate of a polymer.

decomposing the polymer. In the high fluence range the ablation rates of many polymers are similar, as the incident laser light is screened by ablation products and the plasma which are created during the ablation process [82].

4.2.2. Commercially Available and Designed Polymers

Polymer ablation has been a research field for over 20 years, but its full potential for industrial applications has not yet been explored. One possible reason for this is the fact that commercially available polymers, such as polyimide (PI), polymethylmethacrylate (PMMA), and polycarbonate (PC) [102] that are applied in many ablation studies have several drawbacks. These include low sensitivity, carbonization upon irradiation, and redeposition of ablation products on the polymer surface [103].

Therefore, novel photopolymers for laser ablation have been designed. The most important criteria for the designed polymers are:

- High absorption coefficients ($\geq$20,000 cm^{-1}) at the irradiation wavelength.
- Exothermic decomposition at well-defined positions of the polymer backbone.
- Decomposition of the polymer into gaseous products, which are not contaminating the polymer surface [104,105].

An XeCl excimer laser (308 nm, 60 ns) has been selected as irradiation source of this relatively long irradiation wavelength is the possibility to separate the absorption of the photoactive group from other parts of the polymer.

The most promising photopolymers were triazene (-N = N-N<) containing materials, which have high etch rates, low threshold fluences, reveal no surface contamination, and a small heat affected zone [103,106]. The diffractive limited optical resolution which can be achieved by 308 nm irradiation is sufficient for many applications [107].

A typical UV-Vis spectrum (shown in Fig. 2) reveals an absorption band around 196 nm that correspond mainly to the aromatic groups of the polymer. The second strong absorption band at 332 nm corresponds to the triazene chromophore [108]. The chemical structure of a triazene polymer is included as inset in Fig. 2.

An example of the improved ablation quality for the designed polymers is shown in Fig. 3, where the same structure is ablated into a triazene polymer (left) and in polyimide (Kapton™, right). It is noteworthy to mention that both polymers have very similar absorption coefficients at the irradiation wavelength of 308 nm. The structure in the triazene polymer is well defined with no visible debris. For polyimide a pronounced ring of redeposited ablation products can be observed. A closer inspection reveals also contaminations inside the polyimide structure by products that consist mainly of amorphous carbon [106,109–111].

A polyimide with better ablation properties than Kapton™ (Fig. 3 (right)) is Durimid 7020™ (Arch Chemical) (structure shown in Fig. 4) [112]. Durimid belongs

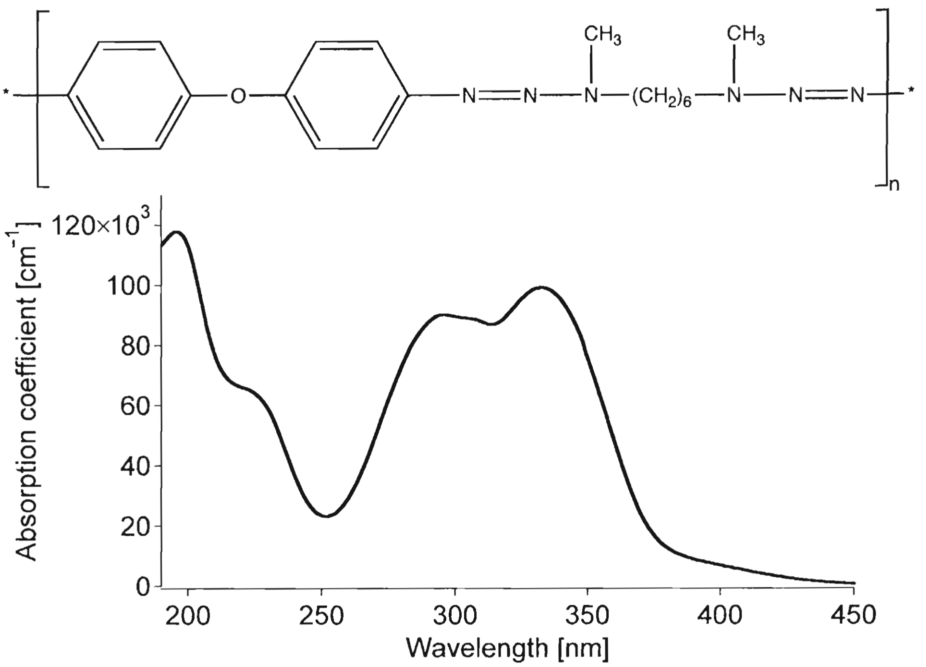


Figure 2: UV-Vis spectrum of a triazene polymer designed for laser ablation at 308 nm and of the chemical structure of the polymer.

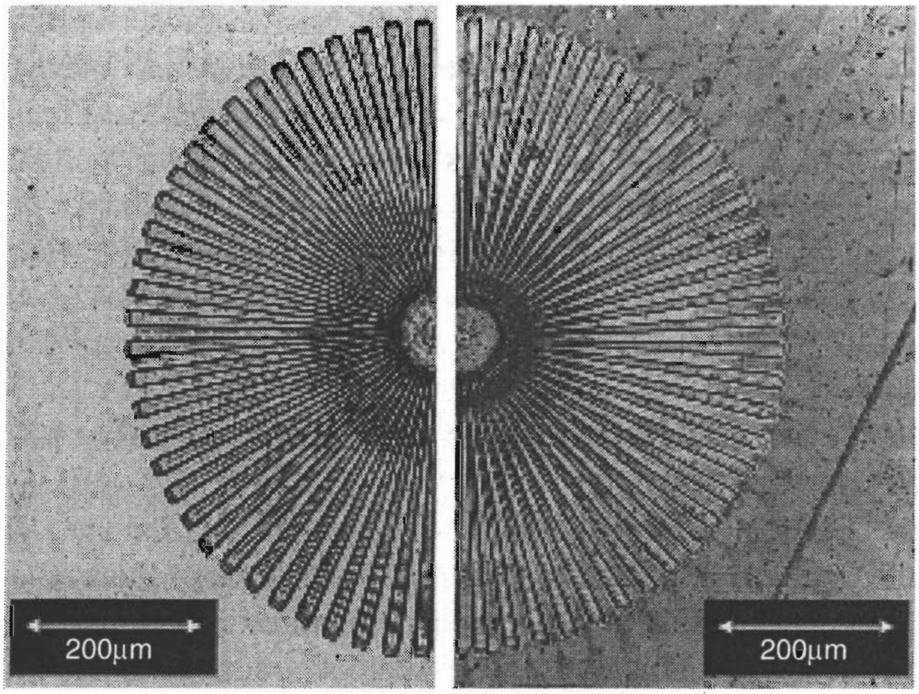
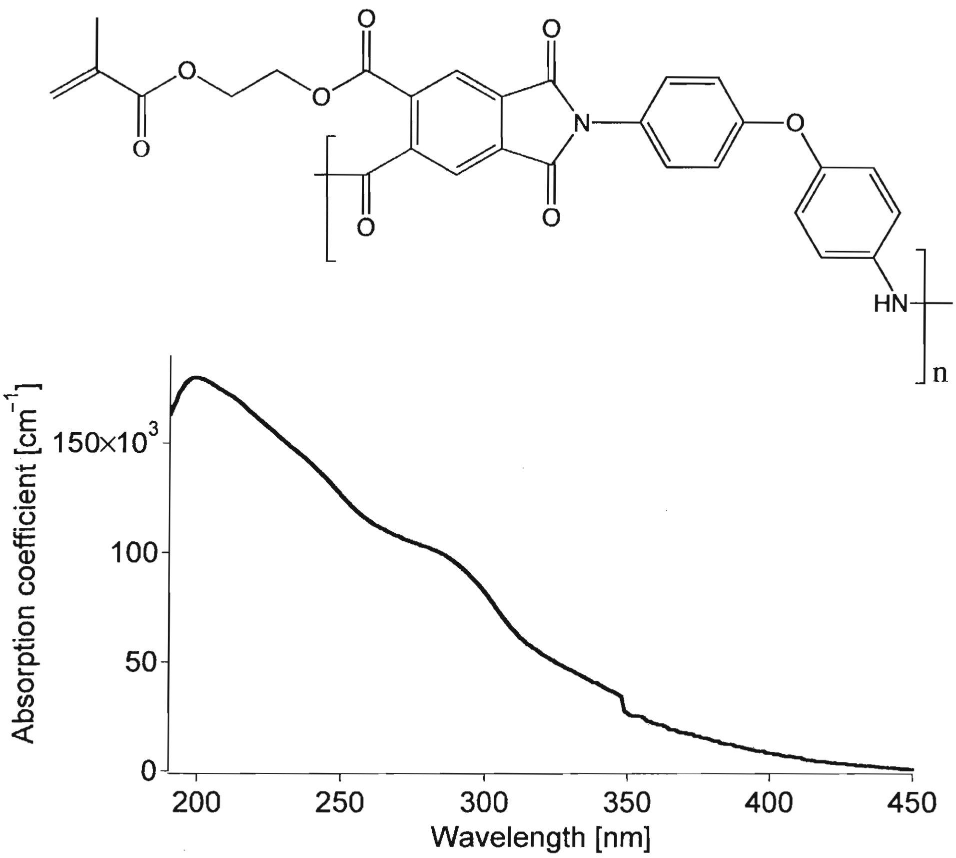


Figure 3: SEM image of a Siemens Star fabricated by laser ablation in a triazene polymer (left) and in polyimide (right) (adapted from [106]).



to the class of photosensitive polyimides, that can be ablated with all common excimer laser. This polymer and other types, such as Pyrolin™ reveals good spin coating properties and have also a linear absorption coefficient (Fig. 4) at 308 nm which is similar to the triazene polymer shown in Fig. 2.

The photosensitive polyimides are after crosslinking, no longer photosensitive and present the typical polyimide properties, i.e. thermal and photo resistance, which makes them suitable materials for optical components in the visible range.

4.3. Methods for the Fabrication of Micro-optical Elements in Polymers

Injection molding is, as discussed in the introduction, one of the key techniques for the low-cost mass production of the complex structures in polymers [4,6,10,15,16]. The principle of these techniques is copying of a surface-relief microstructure of a metal into formable polymers, such as polycarbonate (PC), polymethylmethacrylate (PMMA), polyvinyl chloride (PVC). Hot embossing is mainly used for reproducing submicron grating structures and micro-optics in PC and PVC polymers. The limitation of this method is the depth of the structures, which is about 1 μm [4,15]. Much deeper microstructures (up to 1 mm) in PC or PMMA can be produced by injection molding [4,15]. The replication technology is capable to achieve nanometer resolution over large areas and is in principle a low-production cost process. The major weaknesses of these replication techniques are the limited aspect ratio and depth of the structures, the complex mask which is necessary for producing micro-lens arrays, and the limited number of polymers which can be applied for the replication techniques.

4.3.1. Laser Beam Writing

Laser beam writing techniques, compared to the replication process are more flexible and do not need the complex masks. This technique is based on the sequential patterning of polymer surfaces by a focused laser beam [2,4,7,18–22]. Various type of lasers e.g. cw HeCd, pulsed excimers, and Nd:YAG can be applied as irradiation sources. The fabrication of circular micro-optical elements e.g. spherical shape micro-lenses in polymer samples is achieved by applying a circular mask, which is imaged onto the sample surface. The polymer sample is positioned on a translation stage, which allows to perform circular movement during laser irradiation [4,7,19,20,78]. For the fabrication of an array of micro-lenses in polymers, a two-dimensional array of a circular apertures can be used [19].

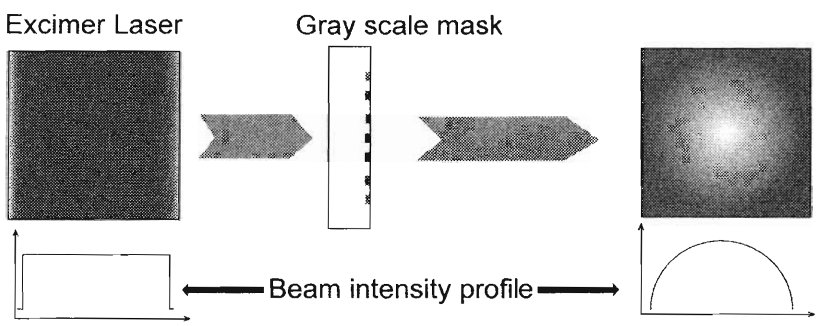
This approach allows a relative fast fabrication of micro-lens arrays in polymers. The advantages of the laser writing technique is its flexibility and that no complex grayscale masks are necessary, but this method is relatively slow compared to replication techniques.

4.3.2. Fabrication of Micro-optics using Laser Ablation and Half Tone or Diffractive Gray Tone Masks

An alternative method to laser writing is the combination of laser ablation with the projection of a half tone (gray tone) mask (as shown in Fig. 5) [25,79, 113–116]. The encoding of the desired structure can be achieved either by a mask with locally variable transmission patterns (the size of the pattern is ≈5 μm) [25,79,113,116].

A half tone (gray scale) mask consists of a number of patterns with chromium layers of various thickness. The modulation of the laser light intensity is based on the local absorption of the laser light by the chromium patterns. One of the major disadvantages of these masks is the low laser damage threshold, which can cause defects in the mask. To overcome this drawback, Smith *et al.* [117,118] invented diffractive phase masks which can be used with high power lasers. Further developments of the DGTPM were performed by David *et al.* [24,119] and Braun *et al.* [120]. A DGTPM is a binary structure fabricated in quartz by *e-beam lithography* and *Reactive Ion Etching* (RIE) which is used to modulate the incoming laser beam intensity [24,120]. No light is absorbed with a DGTPM and, therefore no damage can occur even for very high laser fluences.

The diffractive gray tone masks consist of periodically spaced line structures with various line width. The transmission of the laser light in the zeroth order depends on the ratio between the line width and the grating period, which is also called the duty cycle (DC). Keeping the grating period as a constant and varying the line width allows to continuously change the transmission of the mask (as shown in Fig. 6).



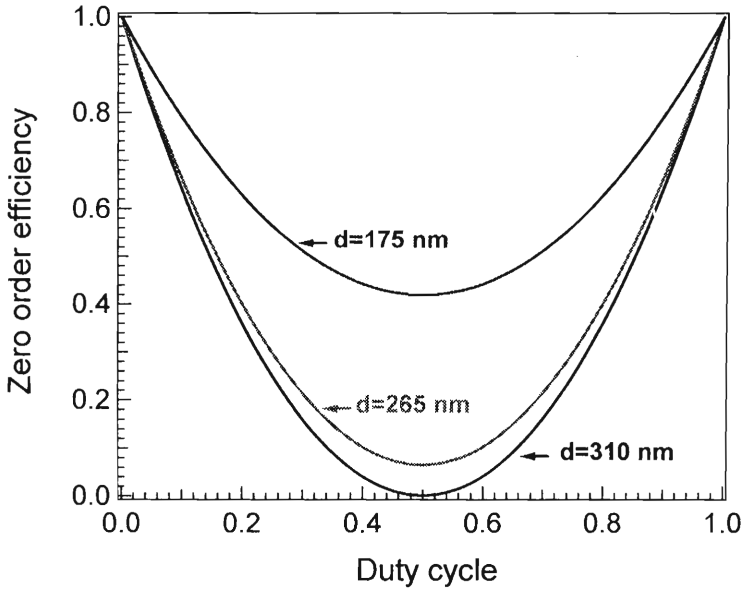


Figure 6: Relation of the Zeroth order efficiency with the duty cycle for a Diffractive Gray Tone Phase Mask.

The transmission (T) of the mask or zero order efficiency can be described by scalar diffraction theory:

$$T = 1 - 2 \cdot DC \cdot (1 - DC) \cdot (1 - \cos\varphi) \tag{2}$$

where DC is the duty cycle and φ is the phase shift.

The zero order efficiency calculated by Equation (2) is close to zero when the phase shift is equal to π and the DC = 0.5. A π phase shift is obtained when the height (h) of the grating structures is equal to $\lambda/(n-1)$, where λ is the laser wavelength and n is refractive index of quartz. A depth of the structure of 310 nm ensures a complete modulation range for an XeCl excimer laser (308 nm, 60 ns) (shown in Fig. 6 as solid line), which is used as irradiation source for all our experiments. The etch rate and threshold fluence of polymers must be included in the DGTPM design to improve the quality of the complex structures ablated into the polymers with a DGTPM. An optimized DGTPM for the fabrication of various structures in one selected polymer has patterns with a depth of 265 nm (instead of 310 nm). The optimization of the masks yields an improvement of the quality of the complex structures [119]. The depth of the features in the DGTPM was even more reduced ($d \approx 175$ nm) for the application of these masks to obtain plano-convex microlenses in quartz. The reason for using a DGTPM, with a typical size of 5 mm, with only half of the modulation depth (shown in Fig. 6) for the fabrication of three-dimensional structures in quartz is the complex etch rate behavior of quartz which is completely different to the laser ablation of polymers. The experimental setup

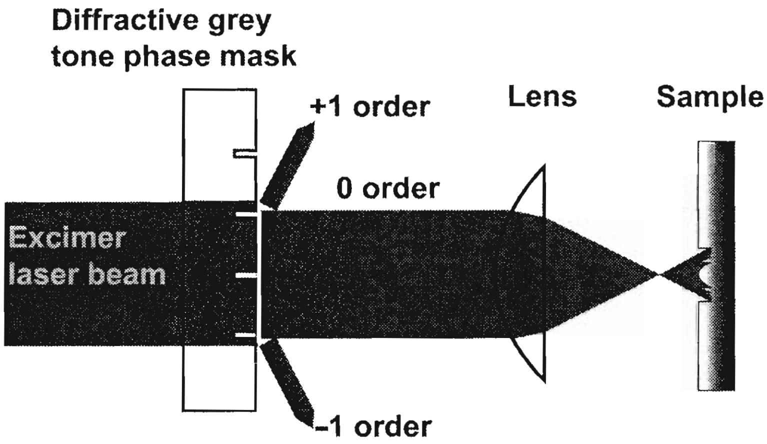
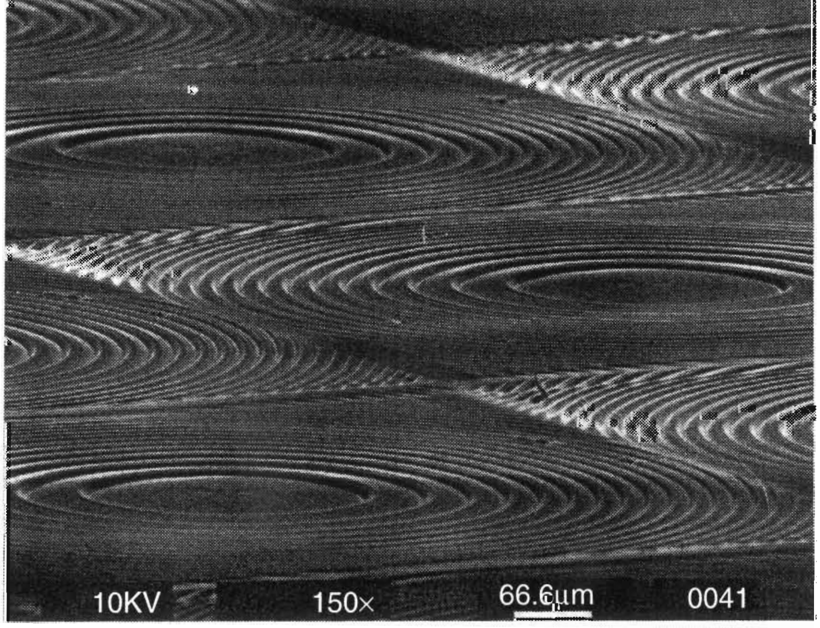


Figure 7: Experimental setup for the fabrication of micro-lenses in polymers.

for the fabrication of complex structures in a photosensitive polyimide (Durimid 7020™) is shown in Fig. 7 and consists of the combination of laser ablation with the projection of a DGTPM.

The intensity of an XeCl excimer is modulated by the DGTPM. The beam is then imaged onto the polymer surface with a 5 times demagnification using a doublet lens. A two-dimensional Fresnel micro-lens array was fabricated in the polyimide (shown in Fig. 8) by moving the sample and repeatedly exposing the DGTPM which encodes the Fresnel lens shape. The size of each micro-lens is 900 × 900 μm.



Such arrays can for example be applied as diffusers, or for beam shaping of white light sources.

One of the advantages of the combination of laser ablation and imaging of the DGTPM compared to the laser writing method is the simple adjustment of the size of the micro-optical elements in the polymers. The same DGTPM can be applied for the fabrication of various sizes of optical components with diameters from 250 μm to several millimeters, by adjusting the demagnification of the DGTPM. A Fresnel lens was transferred in a photosensitive polyimide that was spin-coated onto quartz to test the ability of this method for the fabrication of larger optical components in polymers. The diameter of this lens (shown in Fig. 9A) is 5 mm while the focal length is 32 mm. This lens was fabricated with 40 laser pulses. The depth profile scan of this lens (shown in Fig. 9B) presents the typical features of a Fresnel lens, i.e. parabolic depth profile in the center and triangular shapes on the sides. The size of the optical elements is mainly dependent on the available laser power, which is necessary to induce ablation.

The main disadvantage of the combination of laser ablation with projection of a DGTPM is high cost of the phase mask. The possibility to apply one mask to create various sizes of the micro-optical elements in polymers is a clear advantage to replication techniques, where one mask can be only used for one size of the structure. Another advantage of laser ablation is the fact that most polymers can be structured with UV lasers, especially at 193 nm, while hot embossing and injection molding techniques require thermoplastic or curable polymers that are optimized for the replication process.

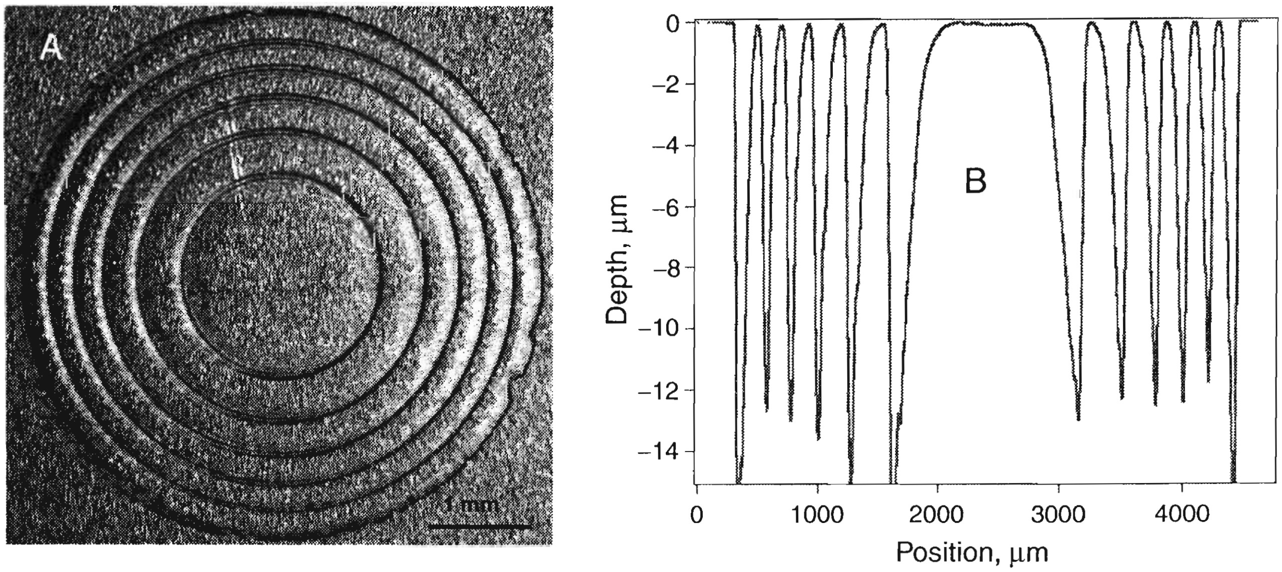


Figure 9: Optical image (A) and line scan (B) of a large Fresnel lens fabricated in Durimid.

4.4. Microstructuring of UV Transparent Materials

UV transparent materials, e.g. quartz, BaF_2, sapphire, etc. are very important in modern optics, mainly due to their wide transparency (from UV to IR), high laser damage threshold (>20 J/cm^2 (at 308 nm)), and high mechanical and chemical stability. One of the commercial applications of micro-lens arrays fabricated in quartz is high power laser beam shaping and homogenizing. However, the fabrication of micro-optics in UV transparent materials is also restricted due to the properties of these materials. Industrial technologies for the fabrication of micro-lens arrays in quartz are based on the combination of photolithography, resist melt-reflow, and RIE [7,34,121–123]. The first step in this approach is the creation of binary cylindrical structures in a photoresist coated on a quartz substrate by photolithography. The two-dimensional features on the sample are converted to three-dimensional by heating the photoresist above the glass transition temperature (>200°C). This results in a flow of the resist to yield the desired spherical shape structures. Finally, the micro-lenses are transferred from the photoresist to the quartz by RIE using a proportional etching process. High-quality refractive micro-lenses with good spherical shape and low etch roughness in quartz can be fabricated by this technique. However, this method has several drawbacks, such as the multiple steps, the necessity for a high control of the proportional etching and resist characteristics, and a relatively slow RIE process (20 nm/min). The drawback of this method resulted in the development of alternative techniques for structuring of UV transparent materials, which are briefly mentioned in the introduction.

Direct laser ablation of quartz can be achieved by ultrafast (femtosecond) lasers. The removal of the material occurs due to the strong multiphoton absorption. A very promising application of femtosecond laser ablation is the three-dimensional microstructuring inside a material [37,44], which can be utilized to create photonic crystals, waveguides, Bragg gratings, etc.

Complex structures with sub-micrometer precision in quartz can be obtained by VUV laser ablation [51,124], where a F_2 excimer laser (157 nm, 11 ns) is used as irradiation source. Well defined structures with the very low etch roughness can be fabricated by this technique in quartz [32,51,52,55]. This method requires transparent gases for the beam path and expensive optics. Fabrication of high quality Fresnel micro-lens arrays in quartz by a focused ion beam was demonstrated by Fu *et al.* [57,125,126]. The drawback of this process is an increase of the absorption in the UV range of the etched areas in quartz due to the exposure of quartz to the Ga^+ ion beam.

Another approach for structuring of UV transparent materials is indirect laser assisted etching using highly absorbing media, which are in contact with the material.

The first application of this approach was performed for the etching of semiconductors materials [59].

Sugioka *et al.* developed a method in which structuring of quartz is assisted by a laser induced plasma [54,60,61,127]. A Nd:YAG laser is applied as an irradiation source, while a metal target, which is in contact with the quartz plate acts as an absorber. The laser light passes through the quartz and is strongly absorbed by the metal target, acts where a plasma is generated. The removal of the quartz is assisted by the plasma process. Well defined gratings in quartz can be prepared by this method, however, the depth of the features is limited to 2 μm.

Another approach for the structuring of sapphire and SiC ceramics with a copper vapor laser (510 nm, 10 ns) laser was demonstrated by Dolgaev *et al.* [64,65,128]. A 0.6 M aqueous CrO_3 solution which is in contact with the sapphire sample was used to achieve the absorption of the laser photons. The key element of the etching process is a temperature jump at the thin sapphire–liquid interface which originates from the strong absorption of the laser light. The rapid rise of the temperature results in heating of the sapphire substrate and thermal decomposition of the solution, which generates non-soluble Cr_2O_3 deposits [129]. These particles form a thin film on the substrate which results in a further increase of the laser induced temperature. The removal of the sapphire is most probably achieved mechanically, resulting from the difference in thermal expansion coefficient between the Cr_2O_3 film and sapphire substrate. A typical etch rate of sapphire with this method is 200 nm per pulse at a laser fluence of 5 J/cm^2. The roughness of the etched features is in the range of several micrometers. The major disadvantage of this method is the high roughness and the deposition of a Cr_2O_3 layer on top of the etched features, which has to be removed by an additional cleaning process.

In 1999, Yabe and coworkers developed a method for precise micromachining of UV transparent materials [69,130]. This technique is similar to the approach of Dolgaev, i.e. in order to increase the absorption of the laser light a strong absorbing organic liquid is used which is in contact with the material. This method has been termed *Laser Induced Backside Wet Etching* (LIBWE) and was applied for the structuring of quartz, CaF_2, BaF_2, and sapphire [62,63,66,69,71,130–136]. Different excimer lasers, i.e. ArF, KrF, XeCl, XeF can be applied as irradiation sources. A number of organic liquids, such as pyrene in acetone (or THF) [31,69,137], aqueous pyranine and naphthalene [63], pure toluene [134,138,139], and naphthalene in methyl-methacrylate [68] can be applied as 'etchant'. An experimental setup for LIBWE is shown in Fig. 10, where an XeCl excimer laser (308 nm, 60 ns) is used as irradiation source with a repetition rate of 5 Hz, while 0.4 M pyrene in acetone and 1.4 M pyrene in tetrahydrofurane were applied as etching media.

A possible mechanism for the LIBWE process is based on the strong absorption of the intense laser light by the organic liquid, which is in contact with the

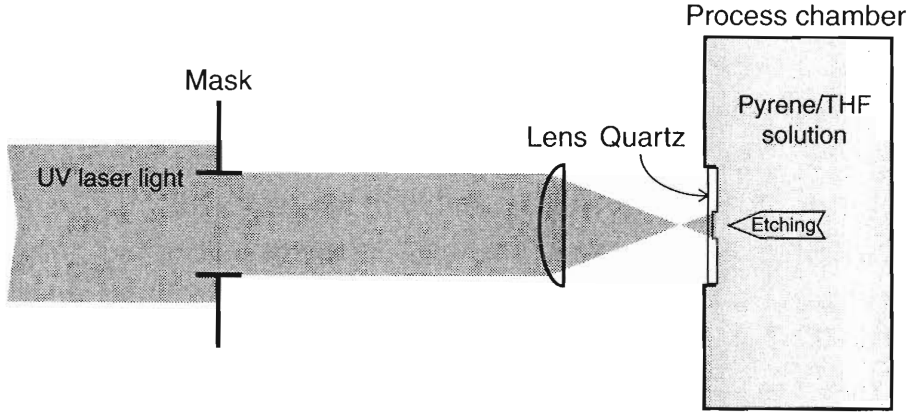


Figure 10: Experimental setup for Laser Induced Backside Wet Etching.

UV transparent material. Rapid relaxation processes of the excited dye molecules generate a fast increase of the temperature at the substrate–liquid interface and may result in softening, melting or even boiling of the UV transparent materials. Secondary processes, which take place at the interphase between the substrate and the liquid, are the creation of a shock wave and the boiling of the solvent. The latter results in the creation of expanding and collapsing bubbles, which generate another strong pressure jump at the interface between the heated material and the liquid. The pressure jump from the shock wave or from the bubble may remove the softened material from the surface [68–70,134,135,137,140].

One characteristic of the structuring of UV transparent materials by LIBWE is the existence of a threshold fluence. The threshold fluence for quartz is defined as the highest fluence, for which no etching can be achieved even if thousands of pulses have to be applied. The threshold fluence is obtained experimentally by measuring the etch rates at various laser fluences (shown in Fig. 11).

The experimentally obtained threshold fluence for quartz using 0.4 M pyrene in acetone solution as etchant is 0.66 J/cm^2, which is much lower than the ablation threshold without solution ($\approx$20 J/cm^2 [142]).

The etching of UV transparent materials by LIBWE is a complex fluence dependent process, which can be divided into several etching regions (marked in Fig. 11 as A, B, C). In the low fluence range the etch rates increases only slowly with an increase of the laser fluence. The roughness of the etched features is in the range of 800 nm and decreases rapidly to 100 nm for higher laser fluences (shown in Fig. 11). Another effect which is observed at these fluences is incubation, which means that the removal of quartz occurs after a number of laser pulses (shown in Fig. 12). Incubation, which is also observed in the case of laser ablation of polymers,

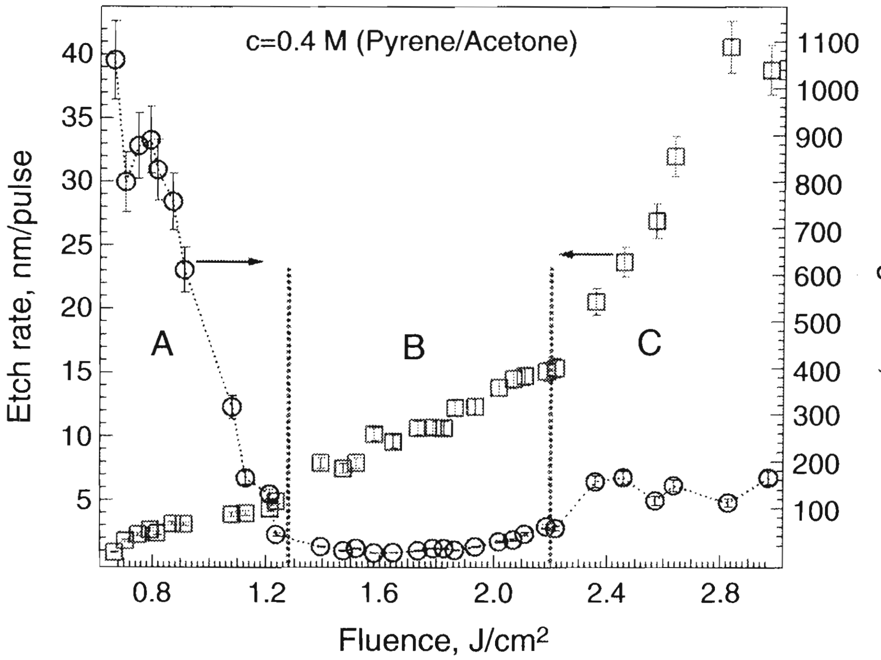


Figure 11: Etch rates and etch roughness of quartz at different laser fluences using a 0.4 M pyrene in acetone solution (irradiation wavelength 308 nm) (adapted from [73]).

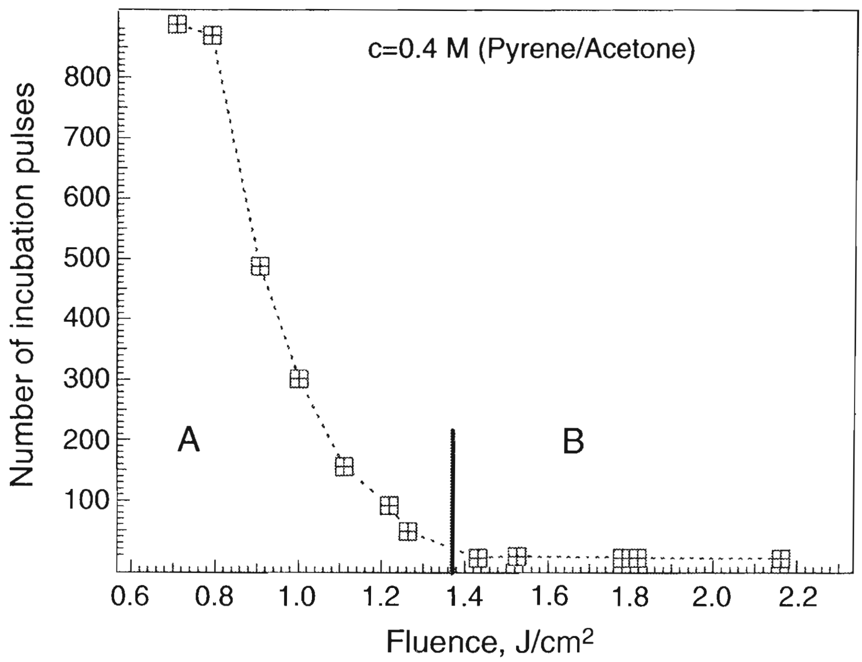


Figure 12: Number of incubation pulses at different laser fluences for a 0.4 M pyrene/acetone solution and 308 nm as irradiation wavelength (adapted from [73]).

On the basis of the experimental results, the following etching mechanism for low laser fluence range can be suggested: the laser induced temperature at the quartz–liquid interface is probably below the melting point of the quartz, but is still high enough to cause boiling of the solution. The pressure waves, generated by the shock wave and collapsing of the laser induced bubbles are also not strong enough to remove the heated material, and no etching occurs. The temperature at the quartz–liquid interface, may however, be high enough to decompose the solution, i.e. solvent or pyrene. This results in the formation of carbon deposits, which strongly adhere to the heated quartz surface [72,131]. The formation of the carbon layer alters the absorption of the laser light, which results in an increase of the temperature jump at the interface between the quartz and the liquid, which is similar to the process described by Dolgaev [65]. The removal of the quartz is possible at the higher temperatures, which may reach the melting point of quartz. Another process which may influence the etching of quartz at the low laser fluences is associated with the mechanical stress, resulting from the different thermal expansion coefficients of quartz and the carbon layer.

The increase of the etch rates with higher laser fluences, i.e. above 1.2 J/cm^2, (marked as B in the Fig. 11), is associated with the generation of higher temperatures at these laser fluences. An increase of the temperature also results in stronger pressure jumps, which remove the softened-molten material yielding smooth etching with a very low etch roughness ($\approx$20 nm). This fluence range is utilized for the fabrication of the micro-optical components in quartz.

A further change of the etch rate is observed for higher fluences (marked as C in Fig. 11) and is accompanied by the formation of a plasma in the solution [73]. The onset of the plasma generation in the solution coincides with the increase of the etch rates but also with an increase of the etch roughness. It is therefore very probable that the plasma assists the etching process but probable in a different way then reported by Sugioka *et al.* [54,60,61,127].

The quality of the etched features in UV transparent dielectrics depends on various etching parameters, such as the laser fluence, pulse number, and concentration of the absorbers (pyrene). In order to obtain the optimum etching conditions for the fabrication of micro-optical elements in quartz different solutions containing various concentrations of absorbers have been studied.

An increase of the pyrene concentration (shown in Fig. 13A) results in the absorption of the laser light in a thinner layer which results in higher temperatures and pressures. The increase of the temperature and pressure jumps is indicated by a shift of the threshold fluence to lower fluences and a reduction of the etch roughness. The number of incubation pulses is also decreasing with an increase of the pyrene concentration [73]. The optimum etching conditions in terms of lowest

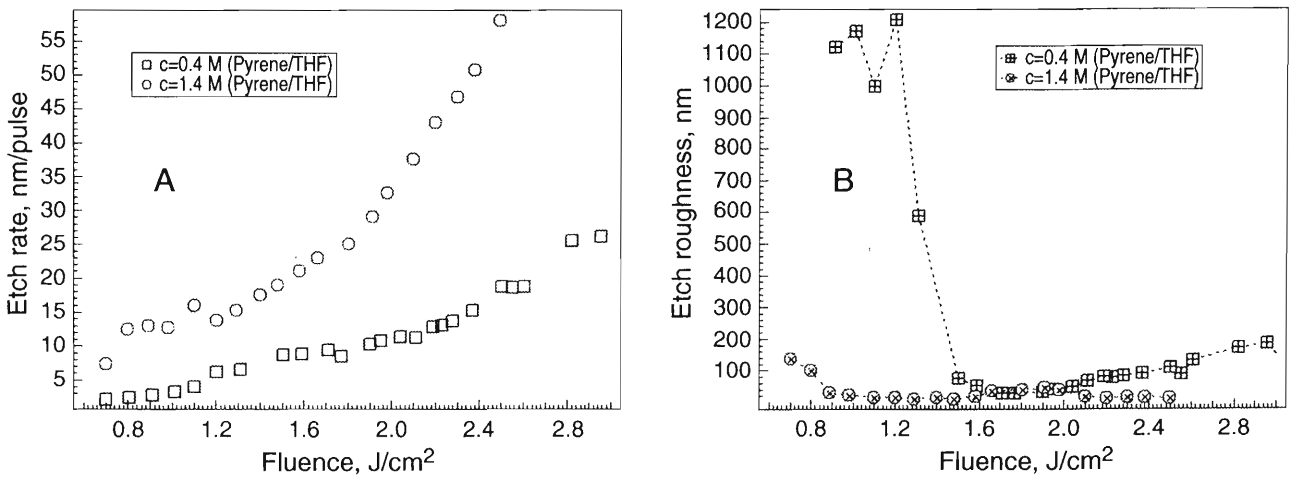


Figure 13: Etch rates (A) and etch roughness (B) of quartz using different concentrations of pyrene in THF (irradiation wavelength 308 nm) (adapted from [73]).

fabrication of micro-optical components in quartz are obtained for a 1.4 M pyrene in THF solution and laser fluences in the range between 0.9–1.6 J/cm^2.

4.4.1. Fabrication and Applications of Micro-optical Elements in Quartz

An array of Fresnel (shown in Fig. 14) and plano-convex (shown in Fig. 15) micro-lenses were fabricated in quartz by the combination of LIBWE and the projecting of a DGTPM. The DGTPM which encodes the Fresnel lens shape was optimized

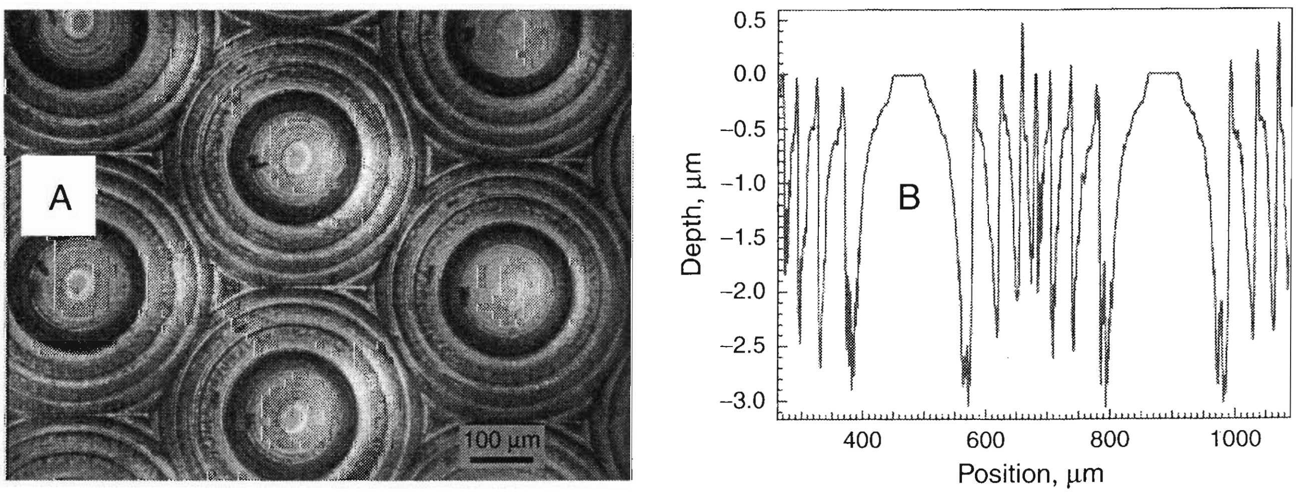


Figure 14: The light microscope image (A) and line scan (B) of a Fresnel micro-lens array fabricated in quartz (adapted from [73]).

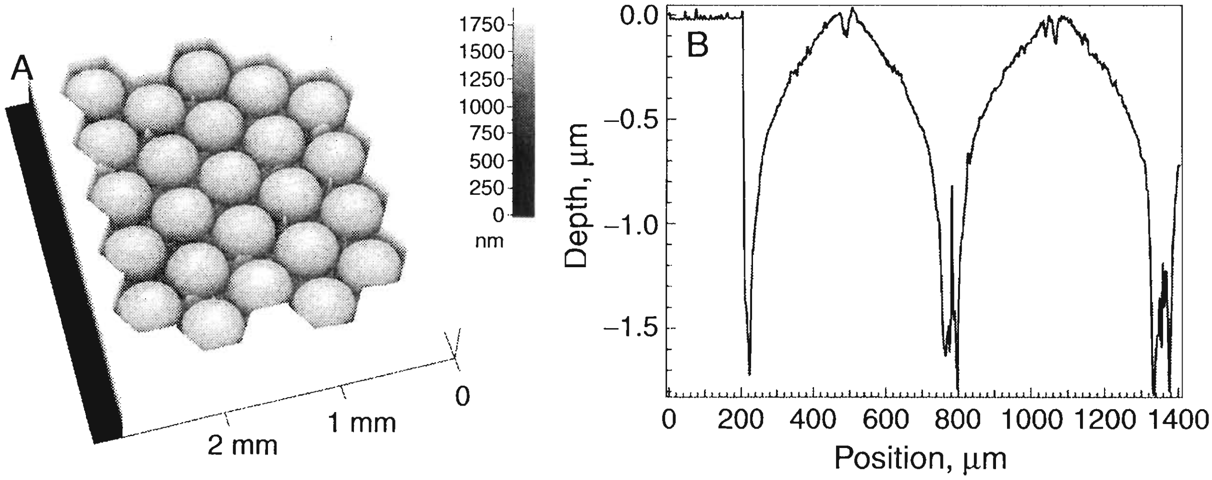


Figure 15: Three dimensional image (A) and horizontal scan (B) of the plano-convex micro-lens array in quartz.

for the fabrication of Fresnel lenses in polymers, which results in the formation of a small plateau in the center of the Fresnel lens in quartz (shown in Fig. 14B). This is caused by the different etch rates and threshold fluences of the photosensitive polyimide compared to quartz.

Another type of micro-lenses, i.e. an array of plano-convex micro-lenses in quartz (shown in Fig. 15) was also fabricated using LIBWE and imaging of a DGTPM. The etch rates and threshold fluence for quartz was included in the design of this DGTPM. The modulation depth of these masks was reduced in order to modulate only the intermediate fluence range (between 0.9–1.6 J/cm^2) where the lowest etch roughness of quartz is observed for a 1.4 M pyrene in THF solution as an etchant.

The focal lengths of the Fresnel and plano-convex micro-lenses are calculated from the depth profile measurements using Equation (3):

$$f = \frac{\left(h_0/2\right) + \left(D^2/8 \cdot h\right)}{2 \cdot (n(\lambda) - 1)} \tag{3}$$

where h_0 is the lens sagitta (the distance from the midpoint of an arc to the midpoint of its chord), D is the diameter of the micro-lens and $n(\lambda)$ is the refractive index of quartz (n = 1.485@308 nm) as a function of the wavelength.

The focal length of the Fresnel micro-lens is 5 mm which corresponds well to the measured value [73]. The focal length of the Fresnel lens is however too small for focal lengths, an optimization of the DGTPM design is necessary, i.e. including the etch parameters into the mask design.

The plano-convex micro-lenses have a much larger focal length ($f = 70$ mm) and are therefore suitable for beam shaping and homogenizing of high-power lasers. Arrays of diffractive and refractive micro-lenses in quartz, as discussed above, are used for the shaping and homogenizing of high-power laser beams. The concept of beam homogenizing is based on splitting of the laser beam intensity into a number of beamlets, which are collected in the focal plane of the collecting lens, as shown in Fig. 16.

The homogenized beam size D obtained at the focal plane of the collecting lens is proportional to the focal length of the collecting lens, the diameter and focal length of the micro-lens, and can be calculated using Equation (4):

$$D = \frac{d_{ul} \cdot F}{f_{ul}} \tag{4}$$

where d_{ul} and f_{ul} are the diameter and the focal length of the micro-lenses, and F is the focal length of the collecting lens.

The homogenizing of a quadrupled Nd:YAG laser beam profile was tested with a quartz micro-lens array which consists of 20 × 22 plano-convex micro-lenses (same as shown in Fig. 15). The focal length of the collecting lens used for the homogenizing of the Nd:YAG laser was 250 mm. The Nd:YAG laser beam profile with and without the beam homogenizer is shown in Fig. 17. The homogenized beam size obtained at the focal plane of the collecting lens is 1.6 mm, which corresponds well to the value calculated from Equation (4).

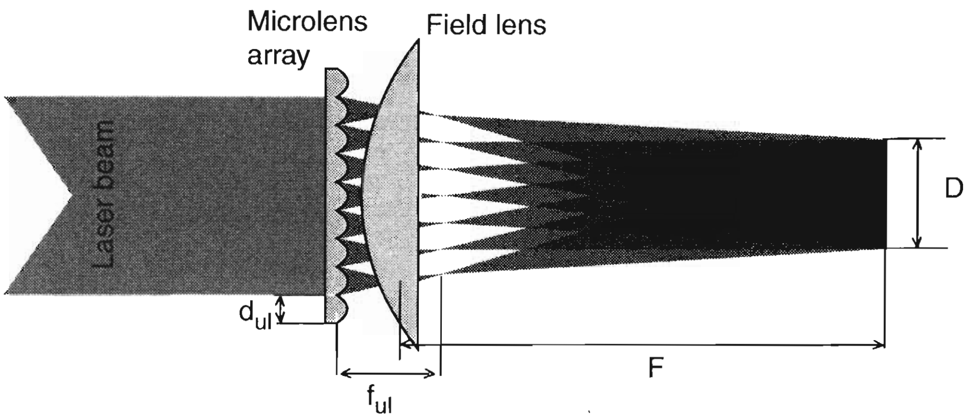


Figure 16: Experimental setup for beam homogenizing (adapted from [72]).

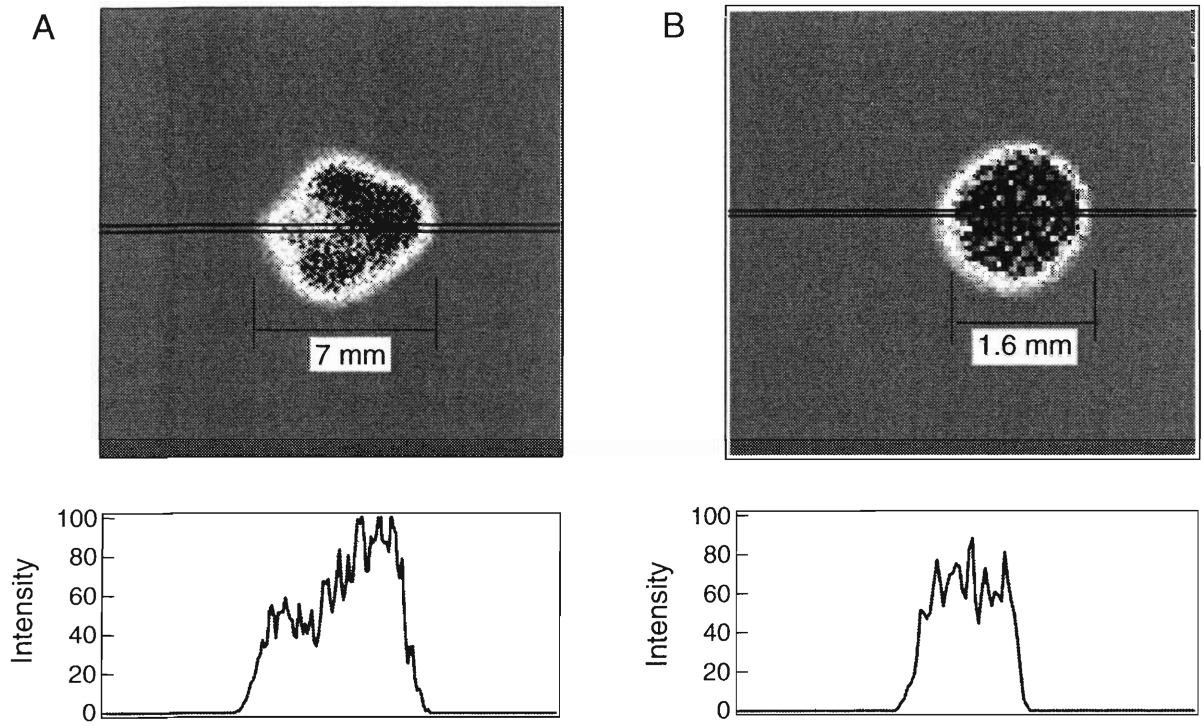


Figure 17: The spatial beam profile of a quadrupled Nd:YAG laser without (A) and with a plano-convex micro-lens array (B).

A clear improvement of the Nd:YAG laser beam profile is obtained when the micro-lens array is applied. However, the line scan profile suggests the existence of energy fluctuation in the intensity of the homogenized laser beam, which is in the range of 30% (RMS). These energy fluctuations are most probably caused by an interference effect, resulting from dividing of the laser beam into a number of beamlets [8,26]. This interference effect is associated with the coherence of the laser and depends on the diameter of the micro-lenses and the focal length of the collecting lens [26]. A further improvement of the micro-lenses is necessary to achieve a more homogenous laser beam profile.

4.5. Conclusions

The development and application of polymers designed specially for laser ablation is a promising approach to optimize the ablation properties, such as reducing the amount of debris and improving the quality of etched surface. Micro-optical elements with dimensions from 250 μm to several millimeters can be fabricated in these polymers by laser ablation and projection of a Diffractive Gray Tone Phase

The combination of Laser Induced Backside Wet Etching (LIBWE) and the projection of a DGTPM can be utilized for the one step fabrication of plano-convex and Fresnel micro-lenses in quartz. Quartz and other UV transparent materials can be structured with this method with fluences well below the damage threshold of these materials. The roughness of the etched features in quartz is low enough to create micro-optical elements that can be applied as beam homogenizers.

A clear improvement of the Nd:YAG laser beam profile laser is obtained for a plano-convex micro-lens array.

References

[1] Dickey, F.M. and Holswade, S.C., Gaussian laser beam profile shaping, *Optical Engineering,* **1996**, *35*(11), 3285–3295.

[2] Gale, M.T., Rossi, M., Pedersen, J. and Schutz, H., Fabrication of continuous-relief micro-optical elements by direct laser writing in photoresists, *Optical Engineering,* **1994a**, *33*(11), 3556–3566.

[3] Herman, P.R., Chen, K.P., Corkum, P.B., Naumov, A., Ng, S. and Zhang, J., Advanced laser microfabrication of photonic components, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2000a**, *4088*, 345–350.

[4] Herzig, H.P., *Micro-optics elements, systems and applications*, Taylor and Francis Ltd., London, **1997**.

[5] Pachauri, J.P., Baby, A., Chaturvedi, M.N., Kothari, H.S., Singh, A. and Singh, B.R., Deep reactive ion etching of silica for planar lightwave circuits using indigenously developed ecr/rie system, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2001**, *4417*, 267–270.

[6] Pasco, I.K. and Everest, J.H., Plastics optics for opto-electronics, *Optics and Laser Technology,* **1978**, *10*(2), 71–76.

[7] Sinzinger, S. and Jahns, J., *Microoptics*, WILEY-VCH, Weinheim GmbH and Co. KGaA, **2003.**

[8] Williams, S.W., Marsden, P.J., Roberts, N.C., Sidhu, J. and Venables, M.A., Excimer laser beam shaping and material processing using diffractive optics, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1998**, *3343*(1–2), 205–211.

[9] Calixto, S. and Sanchez-Martin, F.J., Spherical fused silica microlenses fabricated by the melting method, *Revista Mexicana de Fisica,* **2003**, *49*(5), 421–424.

[10] Cox, W.R., Hayes, D.J., Chen, T., Ussery, D.W., MacFarlane, D.L. and Wilson, E., Fabrication of micro-optics by microjet printing, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1995**, *2383*, 110–115.

[11] Gale, M.T., Rossi, M. and Schutz, H., Fabrication of continuous-relief microoptical elements by direct laser writing in photoresist, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1994b**, *2045*, 54–62.

[12] Jinwon, S., Pitchumani, M., Brown, J., Hockel, H. and Johnson, E.G., Analog micro-optics fabrication by use of a binary phase grating mask, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2004**, *5347*(1), 62–70.
[13] Calixto, S. and Padilla, G.P., Micromirrors and microlenses fabricated on polymer materials by means of infrared radiation, *Applied Optics,* **1996**, *35*(31), 6126–6130.
[14] Fu, Y.Q. and Bryan, N.K.A., Novel one-step method of microlens mold array fabrication, *Optical Engineering*, **2001**, *40*(8), 1433–1434.
[15] Kluepfel, B. and Ross, F., *Holography marketplace: The reference text and directory of the holography industry,* Ross Books, Berkeley, **1991**.
[16] Palermo, P., Korpel, A., Dickinson, G. and Watson, W., Video disc mastering and replication, *Optics and Laser Technology,* **1977**, *9*(4), 169.
[17] Rossi, M. and Saarinen, J., Replication of micro-optics is cost-effective, *Optoelectronics World,* **2002**, *38*(8), S3–S5.
[18] Beinhorn, F., Ihlemann, J., Luther, K. and Troe, J., Micro-lens arrays generated by UV laser irradiation of doped PMMA, *Applied Physics A-Materials Science and Processing,* **1999**, *68*(6), 709–713.
[19] Naessens, K., Ottevaere, H., Baets, R., Van Daele, P. and Thienpont, H., Direct writing of microlenses in polycarbonate with excimer laser ablation, *Applied Optics,* **2003a**, *42*(31), 6349–6359.
[20] Naessens, K., Ottevaere, H., Van Daele, P. and Baets, R., Flexible fabrication of microlenses in polymer layers with excimer laser ablation, *Applied Surface Science,* **2003b**, *208*, 159–164.
[21] Gale, M.T. and Knop, K., The fabrication of fine lens arrays by laser beam writing, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1983**, *398*, 347–353.
[22] Gale, M.T., Rossi, M., Kunz, R.E. and Bona, G.L., Direct laser writing of planar fresnel elements for optical interconnects, *Optical Computing, Proceedings of the International Conference,* **1995**, 267–270.
[23] Ornelas-Rodriguez, M. and Calixto, S., Mid-infrared optical elements fabricated on polymer materials, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2000**, *4087*, 712–719.
[24] David, C., Wei, J., Lippert, T. and Wokaun, A., Diffractive grey-tone phase masks for laser ablation lithography, *Microelectronic Engineering,* **2001**, *57–8*, 453–460.
[25] Borek, G.T., Brown, D.M. and Shafer, J.A., Gray-scale fabrication of micro-optics in bulk zinc selenide and bulk multispectral zinc sulfide, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2004**, *5347*(1), 28–37.
[26] Dickey, F.M. and Holswade, S.C., *Laser Beam Shaping Theory and Techniques,* Marcel Dekker, Inc., New York, **2000**.
[27] Fu, Y.Q., Kok, N. and Bryan, A., Microfabrication of microlens array by focused ion beam technology, *Microelectronic Engineering,* **2000a**, *54*(3–4), 211–221.
[28] He, M., Yuan, X.C., Ngo, N.Q., Bu, J. and Tao, S.H., Single-step fabrication of a microlens array in sol-gel material by direct laser writing and its application in optical

[29] He, M., Yuan, X.C., Ngo, N.Q., Cheong, W.C. and Bu, J., Simple fabrication of cylindrical sol-gel microlens array by reflowing technique, *Optical Engineering,* **2003b**, *42*(8), 2180–2181.
[30] Ihlemann, J. and WolffRottke, B., Excimer laser micro machining of inorganic dielectrics, *Applied Surface Science,* **1996**, *106*, 282–286.
[31] Kopitkovas, G., Lippert, T., David, C., Wokaun, A. and Gobrecht, J., Fabrication of micro-optical elements in quartz by laser induced backside wet etching, *Microelectronic Engineering,* **2003**, *67–8*, 438–444.
[32] Li, J., Herman, P.R., Wei, X.M., Chen, K.P., Ihlemann, J., Marowsky, G., *et al.*, High-resolution F_2-laser machining of micro-optic components, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2002**, *4637*, 228–234.
[33] Romero, L.A. and Dickey, F.M., Lossless laser beam shaping, *Journal of the Optical Society of America A-Optics Image Science and Vision,* **1996**, *13*(4), 751–760.
[34] Savander, P., Microlens arrays etched into glass and silicon, *Optics and Lasers in Engineering,* **1994**, *20*(2), 97–107.
[35] Shealy, D.L. and Dickey, F.M., Laser beam shaping, *Optical Engineering,* **2003**, *42*(11), 3077–3079.
[36] Yuan, X.C., Yu, W.X., Ngo, N.Q. and Cheong, W.C., Cost-effective fabrication of microlenses on hybrid sol-gel glass with a high-energy beam-sensitive gray-scale mask, *Optics Express,* **2002**, *10*(7), 303–308.
[37] Ashkenasi, D., Varel, H., Rosenfeld, A., Henz, S., Herrmann, J. and Cambell, E.E.B., Application of self-focusing of ps laser pulses for three-dimensional microstructuring of transparent materials, *Applied Physics Letters,* **1998**, *72*(12), 1442–1444.
[38] Bruneau, S., Hermann, J., Sentis, M.L., Dumitru, G., Romano, V., Weber, H.P., *et al.*, Femtosecond laser ablation of materials, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2003**, *5147*(1), 199–203
[39] Campbell, E.E.B., Ashkenasi, D. and Rosenfeld, A., Ultra-short-pulse laser irradiation and ablation of dielectrics, in *Lasers in Materials Science,* Vol. 301., (pp. 123–144), Transtec Publications Ltd., Zurich-Uetikon, **1999**.
[40] Henyk, M., Costache, F. and Reif, J., Femtosecond laser ablation from sodium chloride and barium fluoride, *Applied Surface Science,* **2002**, *186*(1–4), 381–384.
[41] Hertel, I.V., Stoian, R., Ashkenasi, D., Rosenfeld, A. and Campbell, E.E., Surface and bulk ultrashort-pulsed laser processing of transparent materials, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2000**, *4088*, 17–24.
[42] Ihlemann, J., Excimer laser ablation of fused-silica, *Applied Surface Science,* **1992**, *54*, 193–200.
[43] Ihlemann, J., Scholl, A., Schmidt, H. and Wolffrottke, B., Nanosecond and femtosecond excimer-laser ablation of oxide ceramics, *Applied Physics A-Materials Science and Processing,* **1995**, *60*(4), 411–417.
[44] Marcinkevicius, A., Juodkazis, S., Watanabe, M., Miwa, M., Matsuo, S., Misawa, H., *et al.*, Femtosecond laser-assisted three-dimensional microfabrication in silica, *Optics Letters,* **2001**, *26*(5), 277–279.

[45] Nagashima, K., Hashida, M., Katto, M., Tsukamoto, M., Fujita, M. and Izawa, Y., Femtosecond laser ablation of Al_2O_3 ceramics, *Transactions of the Institute of Electrical Engineers of Japan, Part C,* **2004**, *124–C*(2), 388–392.

[46] Perry, M.D., Stuart, B.C., Banks, P.S., Feit, M.D., Yanovsky, V. and Rubenchik, A.M., Ultrashort-pulse laser machining of dielectric materials, *Journal of Applied Physics,* **1999**, *85*(9), 6803–6810.

[47] Varel, H., Ashkenasi, D., Rosenfeld, A., Herrmann, R., Noack, F. and Campbell, E.E.B., Laser-induced damage in SiO_2 and CaF_2 with picosecond and femtosecond laser pulses, *Applied Physics A-Materials Science and Processing,* **1996**, *62*(3), 293–294.

[48] Varel, H., Ashkenasi, D., Rosenfeld, A., Wahmer, M. and Campbell, E.E.B., Micromachining of quartz with ultrashort laser pulses, *Applied Physics A-Materials Science and Processing,* **1997**, *65*(4–5), 367–373.

[49] Dyer, P.E. and Walton, C.D., VUV laser ablation of insulators, *Applied Physics A-Materials Science and Processing,* **2004**, *79*(4–6), 721–727.

[50] Herman, P.R., Marjoribanks, R.S., Oettl, A., Chen, K., Konovalov, I. and Ness, S., Laser shaping of photonic materials: Deep-ultraviolet and ultrafast lasers, *Applied Surface Science,* **2000b**, *154*, 577–586.

[51] Ihlemann, J., Muller, S., Pischmann, S., Schafer, D., Wei, M., Li, J., *et al.*, Fabrication of submicron gratings in fused silica by F_2-laser ablation, *Applied Physics A-Materials Science and Processing,* **2003a**, *76*(5), 751–753.

[52] Mi Li, N., Herman, P.R., Nejadmalayeri, A.H. and Jianzhao, L., F_2-laser microfabrication of efficient diffractive optical phase elements, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2004**, *5339*(1) 127–133.

[53] Sugioka, K., Comparison between DUV/VUV and femtosecond laser processing of dielectrics and semiconductors, *Review of Laser Engineering,* **2002**, *30*(5), 226–232.

[54] Sugioka, K., Obata, K., Hong, M.H., Wu, D.J., Wong, L.L., Lu, Y.F., *et al.*, Hybrid laser processing for microfabrication of glass, *Applied Physics A-Materials Science and Processing,* **2003**, *77*(2), 251–257.

[55] Sugioka, K., Obata, K., Midorikawa, K., Hong, M.H., Wu, D. J., Wong, L.L., *et al.*, Microprocessing of glass by hybrid laser processing, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2002**, *4760*, 230–238.

[56] Sugioka, K., Zhang, J. and Midorikawa, K., Hybrid laser processing of micromachining of hard materials, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1999**, *3822*, 6–17.

[57] Fu, Y. and Bryan, N.K.A., Fabrication of three-dimensional microstructures by two-dimensional slice by slice approaching via focused ion beam milling, *Journal of Vacuum Science and Technology B,* **2004**, *22*(4), 1672–1678.

[58] Fu, Y.Q., Kok, N., Bryan, A. and Shing, O.N., Microfabrication of diffractive optical element with continuous relief by focused ion beam, *Microelectronic Engineering,* **2000b**, *54*(3–4), 287–293.

[59] Karlov, N.V., Lukyanchuk, B.S., Sisakyan, E.V. and Shafeev, G.A., Etching of semiconductors by products of the laser thermal-dissociation of molecular gases, *Kvantovaya Elektronika,* **1985**, *12*(4), 803–809.

[60] Jie, Z., Sugioka, K. and Midorikawa, K., Direct fabrication of microgratings in fused quartz by laser-induced plasma-assisted ablation with a KrF excimer laser, *Optics Letters,* **1998**, *23*(18), 1486–1488.

[61] Zhang, J., Sugioka, K. and Midorikawa, K., Laser-induced plasma-assisted ablation of fused quartz using the fourth harmonic of a Nd^{+}:YAG laser, *Applied Physics A-Materials Science and Processing,* **1998b**, *A67*(5), 545–549.

[62] Böhme, R., Zajadacz, J., Zimmer, K. and Rauschenbach, B., Topography and roughness evolution of microstructured surfaces at laser-induced backside wet etching, *Applied Physics A-Materials Science and Processing,* **2005**, *80*(2), 433–438.

[63] Ding, X., Kawaguchi, Y., Niino, H. and Yabe, A., Laser-induced high-quality etching of fused silica using a novel aqueous medium, *Applied Physics A-Materials Science and Processing,* **2002**, *75*(6), 641–645.

[64] Dolgaev, S.I., Lyalin, A.A., Simakin, A.V. and Shafeev, G.A., Fast etching of sapphire by a visible range quasi-cw laser radiation, *Applied Surface Science,* **1996b**, *96–8*, 491–495.

[65] Dolgaev, S.I., Lyalin, A.A., Simakin, A.V., Voronov, V.V. and Shafeev, G.A., Fast etching and metallization of via-holes in sapphire with the help of radiation by a copper vapor laser, *Applied Surface Science,* **1997**, *110*, 201–205.

[66] Kopitkovas, G., Lippert, T., David, C., Wokaun, A. and Gobrecht, J., Surface micromachining of UV transparent materials, *Thin Solid Films,* **2004c**, *453–54*, 31–35.

[67] Niino, H., Ding, X., Kurosaki, R., Narazaki, A., Sato, T. and Kawaguchi, Y., Surface micro-fabrication of uv transparent materials by laser-induced backside wet etching, *CLEO/Pacific Rim 2003, The 5th Pacific Rim Conference on Lasers and Electro-Optics (IEEE Cat. No.03TH8671),* **2003a**, 742–742.

[68] Vass, C., Hopp, B., Smausz, T. and Ignacz, F., Experiments and numerical calculations for the interpretation of the backside wet etching of fused silica, *Thin Solid Films,* **2004a**, *453–54*, 121–126.

[69] Wang, J., Niino, H. and Yabe, A., Micromachining of quartz crystal with excimer lasers by laser-induced backside wet etching, *Applied Physics A-Materials Science and Processing,* **1999a**, *69*, S271–S273.

[70] Wang, J., Niino, H. and Yabe, A., Micromachining of transparent materials with super-heated liquid generated by multiphotonic absorption of organic molecule, *Applied Surface Science,* **2000**, *154*, 571–576.

[71] Zimmer, K. and Böhme, R., Precise etching of fused silica for micro-optical applications, *Applied Surface Science,* **2005**, *243*(1–4), 415–420.

[72] Kopitkovas, G., Lippert, T., David, C., Canulescu, S., Wokaun, A. and Gobrecht, J., Fabrication of beam homogenizers in quartz by laser micromachining, *Journal of Photochemistry and Photobiology A-Chemistry,* **2004a**, *166*(1–3), 135–140.

[73] Kopitkovas, G., Lippert, T., David, C., Sulcas, R., Hobley, J., Wokaun, A.J., *et al.*, Laser micromachining of optical devices, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2004b**, *5662*(1), 515–525.

[74] Srinivasan, R. and Mayne-Banton, V., Self-developing photoetching of poly(ethylene-terephthalate) films by far ultraviolet excimer laser-radiation, *Applied Physics Letters,* **1982**, *41*(6), 576–578.
[75] Kawamura, Y., Toyoda, K. and Namba, S., Effective deep ultraviolet photoetching of polymethyl methacrylate by an excimer laser, *Applied Physics Letters,* **1982**, *40*(5), 374–375.
[76] Aoki, H., U.S. Patent 5736999, **1998**.
[77] Patel, R.S. and Wassick, T.A., *Paper presented at the Proc. SPIE-Int. Soc. Opt. Eng.,* **1997**.
[78] Gale, M.T., Lang, G.K., Raynor, J.M. and Schutz, H., Fabrication of microoptical components by laser beam writing in photoresist, *Proceedings of the SPIE - The International Society for Optical Engineering,* **1991**, *1506*, 65–70.
[79] Quentel, F., Fieret, J., Holmes, A.S. and Paineau, S., Multilevel diffractive optical element manufacture by excimer laser ablation and halftone masks, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2001**, *4274*, 420–431.
[80] Andrew, J.E., Dyer, P.E., Forster, D. and Key, P.H., Direct etching of polymeric materials using a XeCl laser, *Applied Physics Letters,* **1983**, *43*(8), 717–719.
[81] Deutsch, T.F. and Geis, M.W., Self-developing UV photoresist using excimer laser exposure, *Journal of Applied Physics,* **1983**, *54*(12), 7201–7204.
[82] Lazare, S. and Granier, V., Ultraviolet-laser photoablation of polymers - a review and recent results, *Laser Chemistry,* **1989**, *10*(1), 25–40.
[83] Mahan, G.D., Cole, H.S., Liu, Y.S. and Philipp, H.R., Theory of polymer ablation, *Applied Physics Letters,* **1988**, *53*(24), 2377–2379.
[84] Sutcliffe, E. and Srinivasan, R., Dynamics of UV laser ablation of organic polymer surfaces, *Journal of Applied Physics,* **1986**, *60*(9), 3315–3322.
[85] Arnold, N., Luk'yanchuk, B. and Bityurin, N., A fast quantitative modelling of ns laser ablation based on non-stationary averaging technique, *Applied Surface Science,* **1998**, *129*, 184–192.
[86] Cain, S.R., A photothermal model for polymer ablation - chemical modification, *Journal of Physical Chemistry,* **1993**, *97*(29), 7572–7577.
[87] Cain, S.R., Burns, F.C. and Otis, C.E., On single-photon ultraviolet ablation of polymeric materials, *Journal of Applied Physics,* **1992**, *71*(9), 4107–4117.
[88] D'Couto, G.C. and Babu, S.V., Heat-transfer and material removal in pulsed excimer-laser-induced ablation - pulsewidth dependence, *Journal of Applied Physics,* **1994**, *76*(5), 3052–3058.
[89] Luk'yanchuk, B., Bityurin, N., Himmelbauer, M. and Arnold, N., UV-laser ablation of polyimide: From long to ultra-short laser pulses, *Nuclear Instruments and Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* **1997**, *122*(3), 347–355.
[90] Schmidt, H., Ihlemann, J., Wolff-Rottke, B., Luther, K. and Troe, J., Ultraviolet laser ablation of polymers: Spot size, pulse duration, and plume attenuation effects

[91] Srinivasan, V., Smrtic, M.A. and Babu, S.V., Excimer laser etching of polymers, *Journal of Applied Physics,* **1986**, *59*(11), 3861–3867.
[92] Luk'yanchuk, B., Bityurin, N., Anisimov, S., Arnold, N. and Bauerle, D., The role of excited species in ultraviolet-laser materials ablation.3, Non-stationary ablation of organic polymers, *Applied Physics A-Materials Science and Processing,* **1996**, *62*(5), 397–401.
[93] Luk'yanchuk, B., Bityurin, N., Anisimov, S. and Bauerle, D., The role of excited species in UV-laser materials ablation.1, Photophysical ablation of organic polymers, *Applied Physics A-Materials Science and Processing,* **1993**, *57*(4), 367–374.
[94] Bityurin, N., Malyshev, A., Luk'yanchuk, B., Anisimov, S. and Bäuerle, D., *Paper presented at the Proc. SPIE.*, **1996**.
[95] Bityurin, N., UV etching accompanied by modifications, Surface etching, *Applied Surface Science,* **1999**, *139*, 354–358.
[96] Treyz, G.V., Scarmozzino, R. and Osgood, R.M., Deep ultraviolet laser etching of vias in polyimide films, *Applied Physics Letters,* **1989**, *55*(4), 346–348.
[97] Srinivasan, R. and Braren, B., Ultraviolet-laser ablation of organic polymers, *Chemical Reviews,* **1989**, *89*(6), 1303–1316.
[98] Küper, S., Brannon, J. and Brannon, K., Threshold behavior in polyimide photoablation - single-shot rate measurements and surface-temperature modelling, *Applied Physics A-Materials Science and Processing,* **1993**, *56*(1), 43–50.
[99] Arnold, N. and Bityurin, N., Model for laser-induced thermal degradation and ablation of polymers, *Applied Physics A-Materials Science and Processing,* **1999**, *68*(6), 615–625.
[100] Srinivasan, R. and Braren, B., Ablative photodecomposition of polymer-films by pulsed far-ultraviolet (193 nm) laser-radiation – dependence of etch depth on experimental conditions, *Journal of Polymer Science Part A-Polymer Chemistry,* **1984**, *22*(10), 2601–2609.
[101] Srinivasan, R., Braren, B. and Casey, K.G., Nature of incubation pulses in the ultraviolet-laser ablation of polymethyl methacrylate, *Journal of Applied Physics,* **1990**, *68*(4), 1842–1847.
[102] Suzuki, K., Matsuda, M., Ogino, T., Hayashi, T., Terabayashi, T. and Amemiya, K., *Paper presented at the Proc. SPIE,* **1997**.
[103] Lippert, T., Hauer, M., Phipps, C.R. and Wokaun, A., Fundamentals and applications of polymers designed for laser ablation, *Applied Physics A-Materials Science and Processing,* **2003**, *77*(2), 259–264.
[104] Bennett, L.S., Lippert, T., Furutani, H., Fukumura, H. and Masuhara, H., Laser induced microexplosions of a photosensitive polymer, *Applied Physics A-Materials Science and Processing,* **1996**, *63*(4), 327–332.
[105] Lippert, T., Langford, S.C., Wokaun, A., Savas, G. and Dickinson, J.T., Analysis of neutral fragments from ultraviolet laser irradiation of a photolabile triazeno polymer, *Journal of Applied Physics,* **1999a**, *86*(12), 7116–7122.
[106] Lippert, T. and Dickinson, J.T., Chemical and spectroscopic aspects of polymer ablation: Special features and novel directions, *Chemical Reviews,* **2003**, *103*(2), 453–485.

[107] Lippert, T., David, C., Hauer, M., Wokaun, A., Robert, J., Nuyken, O., *et al.*, Polymers for UV and near-IR irradiation, *Journal of Photochemistry and Photobiology A-Chemistry,* **2001**, *145*(1–2), 87–92.
[108] Lippert, T., Bennett, L.S., Nakamura, T., Niino, H., Ouchi, A. and Yabe, A., Comparison of the transmission behavior of a triazeno-polymer with a theoretical model, *Applied Physics A-Materials Science and Processing,* **1996**, *63*(3), 257–265.
[109] Lippert, T., Dickinson, J.T., Hauer, M., Kopitkovas, G., Langford, S.C., Masuhara, H., *et al.*, Polymers designed for laser ablation-influence of photochemical properties, *Applied Surface Science,* **2002**, *197*, 746–756.
[110] Lippert, T., Ortelli, E., Panitz, J.C., Raimondi, F., Wambach, J., Wei, J., *et al.*, Imaging-XPS/Raman investigation on the carbonization of polyimide after irradiation at 308 nm, *Applied Physics A-Materials Science and Processing,* **1999b**, *69*, S651–S654.
[111] Raimondi, F., Abolhassani, S., Brutsch, R., Geiger, F., Lippert, T., Wambach, J., *et al.*, Quantification of polyimide carbonization after laser ablation, *Journal of Applied Physics,* **2000**, *88*(6), 3659–3666.
[112] Brannon, J.H., Lankard, J.R., Baise, A.I., Burns, F. and Kaufman, J., Excimer laser etching of polyimide, *Journal of Applied Physics,* **1985**, *58*(5), 2036–2043.
[113] Braun, A., Zimmer, K. and Bigl, F., Combination of contour and half-tone masks used in laser ablation, *Applied Surface Science,* **2000**, *168*(1–4), 178–181.
[114] Daschner, W., Long, P., Stein, R., Wu, C. and Lee, S.H., Cost-effective mass fabrication of multilevel diffractive optical elements by use of a single optical exposure with a gray-scale mask on high-energy beam-sensitive glass, *Applied Optics,* **1997**, *36*(20), 4675–4680.
[115] Suleski, T.J. and Oshea, D.C., Gray-scale masks for diffractive-optics fabrication:1, Commercial slide imagers, *Applied Optics,* **1995**, *34*(32), 7507–7517.
[116] Zimmer, K., Braun, A. and Bigl, F., Combination of different processing methods for the fabrication of 3d polymer structures by excimer laser machining, *Applied Surface Science,* **2000**, *154*, 601–604.
[117] Smith, A.H. and Hunter, R.O.Jr., High power phase masks for imaging systems, U.S. Patent 5328785, **1992**.
[118] Smith, A.H., Hunter, R.O.Jr. and McArthur, B.B., High power masks and methods for manufacturing same, U.S. Patent 5501925, **1994**.
[119] David, C. and Hambach, D., Line width control using a defocused low voltage electron beam, *Microelectronic Engineering,* **1999**, *46*(1–4), 219–222.
[120] Braun, A. and Zimmer, K., Diffractive gray scale masks for excimer laser ablation, *Applied Surface Science,* **2002**, *186*(1–4), 200–205.
[121] He, M., Yuan, X., Ngo, N.Q., Cheong, W.C. and Jing, B., Reflow technique for the fabrication of an elliptical microlens array in sol-gel material, *Applied Optics,* **2003a**, *42*(36), 7174–7178.
[122] Herzig, H.P., Schilling, A., Stauffer, L., Vokinger, U. and Rossi, M., Efficient

[123] Nussbaum, P., Volkel, R., Herzig, H.P., Eisner, M. and Haselbeck, S., Design, fabrication and testing of microlens arrays for sensors and microsystems, *Pure and Applied Optics,* **1997**, *6*(6), 617–636.

[124] Ihlemann, J., Muller, S., Puschmann, S., Schafer, D., Herman, P.R., Jianzhao, L., *et al.*, F_2-laser microfabrication of sub-micrometer gratings in fused silica, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2003b**, *4941*, 94–98.

[125] Fu, Y.Q. and Bryan, N.K.A., Investigation of integrated diffractive/refractive microlens microfabricated by focused ion beam, *Review of Scientific Instruments,* **2000**, *71*(6), 2263–2266.

[126] Fu, Y.Q., Bryan, N.K.A. and Zhou, W., Quasi-direct writing of diffractive structures with a focused ion beam, *Optics Express,* **2004**, *12*(9), 1803–1809.

[127] Zhang, J., Sugioka, K. and Midorikawa, K., High-speed machining of glass materials by laser-induced plasma-assisted ablation using a 532-nm laser, *Applied Physics A-Materials Science and Processing,* **1998a**, *A67*(4), 499–501.

[128] Dolgaev, S.I., Lyalin, A.A., Shafeev, G.A. and Voronov, V.V., Fast etching and metallization of sic ceramics with copper-vapor-laser radiation, *Applied Physics A-Materials Science and Processing,* **1996a**, *63*(1), 75–79.

[129] Dolgaev, S.I., Kirichenko, N.A. and Shafeev, G.A., Deposition of nanostructured Cr_2O_3 on amorphous substrates under laser irradiation of the solid-liquid interface, *Applied Surface Science,* **1999**, *139*, 449–454.

[130] Wang, J., Niino, H. and Yabe, A., One-step microfabrication of fused silica by laser ablation of an organic solution, *Applied Physics A-Materials Science and Processing,* **1999b**, *68*(1), 111–113.

[131] Böhme, R., Spemann, D. and Zimmer, K., Surface characterization of backside-etched transparent dielectrics, *Thin Solid Films,* **2004**, *453–54*, 127–132.

[132] Böhme, R. and Zimmer, K., Low roughness laser etching of fused silica using an adsorbed layer, *Applied Surface Science,* **2004**, *239*(1), 109–116.

[133] Ding, X.M., Sato, T., Kawaguchi, Y. and Niino, H., Laser-induced backside wet etching of sapphire, *Japanese Journal of Applied Physics Part 2-Letters,* **2003**, *42*(2B), L176–L178.

[134] Kawaguchi, Y., Ding, X., Narazaki, A., Sato, T. and Niino, H., Transient pressure induced by laser ablation of liquid toluene: Toward the understanding of laser-induced backside wet etching, *Applied Physics A-Materials Science and Processing,* **2004**, *79*(4–6), 883–885.

[135] Vass, C., Smausz, T. and Hopp, B., Wet etching of fused silica: A multiplex study, *Journal of Physics D-Applied Physics,* **2004b**, *37*(17), 2449–2454.

[136] Zimmer, K., Böhme, R., Braun, A., Rauschenbach, B. and Bigl, F., Excimer laser-induced etching of sub-micron surface relief gratings in fused silica using phase grating projection, *Applied Physics A-Materials Science and Processing,* **2002**, *74*(4), 453–456.

[137] Böhme, R., Braun, A. and Zimmer, K., Backside etching of UV-transparent materials at the interface to liquids, *Applied Surface Science,* **2002**, *186*(1–4), 276–281.

[138] Kawaguchi, Y., Ding, X., Narazaki, A., Sato, T. and Niino, H., Transient pressure induced by laser ablation of toluene, a highly laser-absorbing liquid, *Applied Physics A-Materials Science and Processing,* **2005**, *80*(2), 275–281.

[139] Zimmer, K., Böhme, R. and Rauschenbach, B., Laser etching of fused silica using an absorbed toluene layer, *Applied Physics A-Materials Science and Processing,* **2004**, *79*(8), 1883–1885.

[140] Niino, H., Yasui, Y., Ximing, D., Narazaki, A., Sato, T., Kawaguchi, Y., *et al.*, Surface microfabrication of silica glass by excimer laser irradiation of toluene solution, *Proceedings of the SPIE - The International Society for Optical Engineering,* **2003b**, *4977*, 269–280.

[141] Duley, W.W., *Uv Lasers: Effects and Applications in Materials Science,* Press Syndicate of the University of Cambridge, Cambridge, **1996**.