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Laser-assisted etching of borosilicate glass in potassium hydroxide

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Abstract: We present a method for the selective etching of borosilicate glass (SCHOTT Borofloat 33), in which we modify the glass with an ultrashort pulse laser and subsequent wet chemical etching. The BF33 glass is often used in microtechnology to produce sensors, actors, and fluidic chips as it can be bonded to silicon wafers by anodic bonding. The glass is irradiated and modified by circular polarized laser light with a wavelength of 1030 nm. By etching the glass with potassium hydroxide, the modified material can be removed. In this study, the selectivity was analyzed dependent on the laser parameters pulse repetition rate, pulse duration, writing speeds, and pulse energy. A selectivity up to 540 could be observed in this study. Finally, the manufacturing capabilities for three-dimensional free form shapes in BF33 are demonstrated and compared with fused silica.

1. Introduction

Selective laser-assisted chemical etching (SLE) is a bulk micromachining technology for transparent materials. The technology uses a strongly focused laser spot for writing structures into the volume of a glass substrate. These structures are subsequently removed from the substrate. Compared to classical lithography based glass etching processes, this concept has the advantage that three-dimensional shapes can be fabricated [1]. As a result of the light matter interaction, nano-gratings and/or nano-porosities result in the material [2]. The modified volume can be removed by subsequent wet chemical etching.

A large number of publications is available on the SLE processing of FOTURAN and Fused Silica [3,4]. The technology was also further developed for other materials like alumnia-borosilicate glass [5], BK7 [6], sapphire [7] and borosilicate glass [8]. Borosilicate glasses like Borofloat 33, MEMpax from SCHOTT or PYREX from Corning are often used in classical microtechnology, as they can be anodically bonded with silicon, which makes them highly interesting for micro-electro-mechanical-systems (MEMS) and fluidic microsystems.

Matsuo et al. have shown that it is possible to apply the selective laser etching with potassium hydroxide (KOH) on borosilicate glasses like PYREX [8]. They reported selectivities up to 500 by using a microscope objective with a magnification of 100x and a numerical aperture (NA) of 1.35. The current study investigates the selective laser etching of SCHOTT BF33. The glass morphology is modified with a focused femtosecond laser source and subsequently etched with KOH. We could show that it is possible to achieve a high etching selectivity by using an objective with a magnification of 20x and a NA of 0.4 in combination with high writing velocities. In addition, we demonstrated the three-dimensional shaping capabilities of the BF33 etching process compared to the reference material Fused Silica.

2. Experimental setup

The manufacturing process for laser-induced selective chemical etching (SLE) is based on two main production steps. In a first step, the glass morphology is modified by the applied ultrashort laser pulse (Section 2.1, Fig. 1(a)) and in a second step the glass substrate is shaped

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by wet chemical etching (Section 2.2). For the SLE process, different laser writing parameters have a great influence on the result of the subsequent etching process, regarding etching rates, selectivity, surface roughness, etc. The influence of different laser parameters can therefore only be assessed indirectly based on the etching results. A first scan of the parameter field was done by characterizing through holes in glass (Section 2.3, Fig. 1(b)). The selectivity of the etching process was investigated by measuring the etching rate of the modified and unmodified material for the selected parameter field (Section 2.4, Fig. 1(c)). The potential of BF33 for the manufacturing of three-dimensional shaped components was demonstrated on different test geometries and compared with respective reference structures in Fused Silica (Section 2.5, Fig. 1(d)).

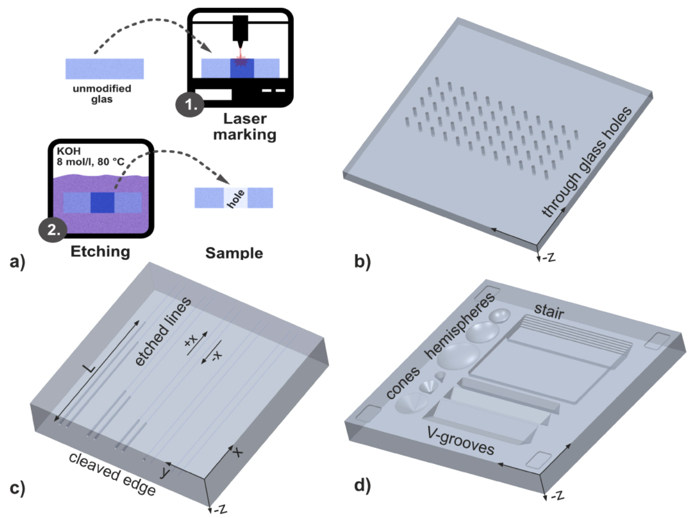

Fig. 1. a) illustration of the selective laser etching process b) through holes in glass; c) laser written lines after etching; d) geometries and shapes that were used to demonstrate 3D capabilities.

2.1. Laser setup for material modification

The glass modification is induced by focusing a femtosecond laser into the substrate and moving the focus inside the material along predefined paths. The modification process inside the glass depends on various laser parameters like pulse repetition rate, pulse duration and pulse energy. In our laser configuration the pulse duration can be tuned from 300 fs to 10 ps. In addition, the pulse repetition rate can be adjusted from a single pulse to a repetition rate of 10 MHz. The linearly polarized laser delivers a beam with a wavelength of 1030 nm which is circular polarized by a quarter waveplate. A microscope objective with a NA of 0.4, a magnification of 20x and a cover glass correction of 1.1 mm is used to focus the laser beam into the substrate.

The controlled movement of the substrate with a 3-axis linear stage system (x, y, z) enables the writing of user defined lines and structures into the substrate. The setup is additionally equipped with a galvanometer scanner which allows the deflection of the laser beam in the field of view of the objective. The galvanometer scanner setup is used for the writing of three-dimensional shapes. If the 3D structures are larger than the field of view, stitching with the 3-axis linear stage is used in addition.

All preliminary described components are integrated in the laser machining platform from LightFab, which is used in this study to manufacture the three-dimensional shapes and modification lines.

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2.2. Wet chemical etching of laser induced modifications

After the laser treatment the glass substrate is wet-chemically etched with potassium hydroxide (KOH). The KOH solution has a concentration of 8.5 ± 0.5 mol/l and is heated up to a temperature of 80±3°C For the heating a temperature controlled ultrasonic bath with a temperature fluctuation smaller than 0.5°C is used. The substrate and KOH solution are enclosed in a separate container, which is placed in the heated water bath.

Fresh unused KOH solutions were used for all investigations, to prevent micro-masking effects, causing randomly localized rough surface areas. In addition, the containers were properly cleaned before reusing them.

2.3. Parameter study on through holes in glass

The parameter range of the laser machining system is enormous. For this reason, through holes were written into 500 μm thick glass substrates using different pulse repetition rates, pulse durations, pulse energies and writing speeds. Lancry et al. demonstrated the formation of nanogratings respectively nano-porosities for pulse energies of 1000 nJ and repetition rates lower than 250 kHz [2] in borosilicate glasses. The parameter variation for pulse duration and writing speeds was chosen according to these results, preliminary tests and reference parameters in Fused Silica. The laser parameters used are summarized in Table 1.

Table 1. Test parameters of the parameter study for through holes in glass

parameter	unit	values
rep.rate	kHz	52, 105, 149 and 249
pulse duration	ps	1 – 10 (in 1 ps steps)
pulse energy	nJ	≤ 1200
writing speed	mm/s	25, 75, 125 and 150
etch time	min	50 - 150 (in steps of 25 min)

For through hole generation, circles with a diameter of 300 μm and a vertical distance Δz of 5 μm were written into the glass with different laser parameter combinations. The slicing procedure used to generate the circles is illustrated in Fig. 2. After the writing sequence, the substrates were etched with KOH and the resulting holes were analyzed using an optical microscope. Different etching times (according to Table 1) were used to determine the etching rate.

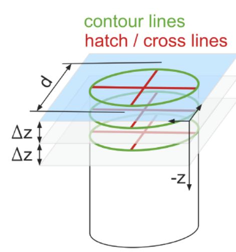

Fig. 2. Sketch of the slicing procedure used to translate the 3D shapes to laser writing curves.

2.4. Determination of etching selectivity

For the determination of the selectivity of our KOH process, the etching rate r_1 of modified and r_0 of unmodified glass were measured. The etching selectivity represents the ratio of these two values via the formula $S = (r_1 + r_0)/r_0$.

For the measurement of the etching rate r_1, channel structures inside the glass volume are often used [9–12]. To generate such channels, lines were written below the surface in forward and reverse direction using the linear axis of the laser machining system. After completion of the laser writing process, the substrate was cleaved twice and was etched in KOH for 4 hours (t_e =230 min). The etching rate r_1 of the modified glass material can be calculated by measuring the length L of the etched channel, giving $r_1 = L/t_e$. The length L was measured by transmission-light microscopy.

Additionally, the etching rate r_0 of the unmodified material has to be determined. This was done by a thickness measurement of the substrate before and after the wet etching process. The etching rate can be calculated using the following formula $r_0 = \Delta d_{sub}/(2t_e)$, where Δd_{sub} is the substrate thickness reduction due to the etching.

2.5. Demonstration and comparison of 3D shape manufacturing capabilities

To demonstrate the potential of BF33 for the manufacturing of three-dimensional shaped components, test structures like hemispheres, V-grooves, cones and a stair were written and etched into BF33 and Fused Silica. These test structures are illustrated in Fig. 1(d).

Three-dimensional shapes have to be translated to writing paths for the laser writing process. These writing paths are generated by slicing the shapes in the z direction into planes with a spacing Δz of 5 μm. In all these planes the contours lines of the shapes are calculated. In addition, all the structures that have to be removed are hatched and filled with a square grid at each plane with a line distance of 300 μm. In a next step the contours are filled with lines with a lateral (xy) spacing of 5 μm on every 10th plane. Finally, during the etching, small glass cubes are released with a size of 300x300x50 μm^3. If the distance between the contour lines gets larger than about 10 μm, the etching process will no longer work properly. Therefore the slicing distance Δz of the contours in the lower part of the hemispheres is reduced to 1 μm.

Depending on the focus penetration into the glass, the laser objective shows spherical aberrations which enlarge the focus diameter. For that reason, a depth dependent laser power correction is used to write three-dimensional shapes. The minimum laser power is defined to be in a depth of 1.1 mm since the spherical aberrations of the objective are corrected for a cover glass thickness of 1.1 mm. If the laser focus is below or above the 1.1mm the pulse power is linearly increased.

For the manufacturing of 3D shapes in Fused Silica, process parameters were used that were published by Gottmann and Hermans et al. [12,13]. The shapes in BF33 were manufactured with the parameter set determined in this publication.

Finally, the dimensions and geometries of the manufactured structures in Fused Silica and BF33 were characterized by focus variation (Alicona InfiniteFocus G5) and compared with each other.

3. Results

In the following sections the results of the parameter study for the through holes in glass, the selectivity results and the comparison of 3D structures in Fused Silica and BF33 are presented.

3.1. Parameter study using through holes in glass

The goal of the parameter study is the determination of optimal laser processing parameters for the borosilicate glass BF33. By analyzing the etch results of the through holes in glass after 50, 75, 100 and 150 minutes the etching rates r for different sets of laser parameters were measured.

With an etching time of 50 minutes no complete etching through the glass was visible. Consequently, all etching rates must be smaller than 300 μm/h. By increasing the etching time to 75 min, first through holes in glass could be observed. This etching time corresponds to an etch rate which is greater than 200 μm/h. Figure 3 shows a microscope image of an etched substrate.

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The black circles are successfully etched through holes. The circles marked with crosses are not completely etched holes.

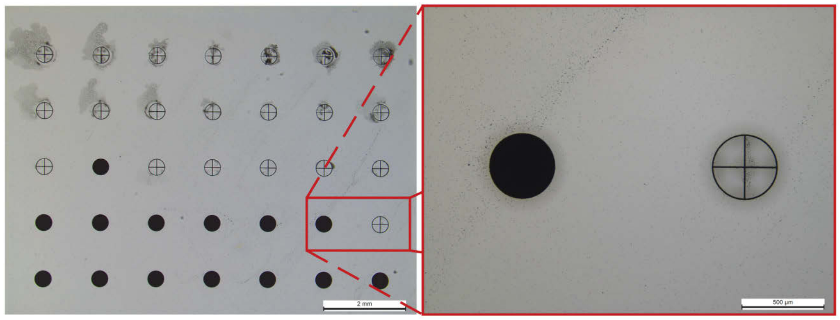

Fig. 3. Bright field microscope image of an etched borosilicate substrate. The dark holes represent completely etched through holes in glass. The crosses enclosed by circles indicate the laser writing contours i.e. the incompletely etched through holes.

Figure 4 shows the dependence of the etch rate r as a function of writing speed v, repetition rate R, pulse duration τ and pulse energy E. The color of the dots indicate the highest etch rate achieved in the sub-parameter space, meaning that all the results for different parameters are included in the graphs, but only the result with the highest etch rate for one parameter pair is shown.

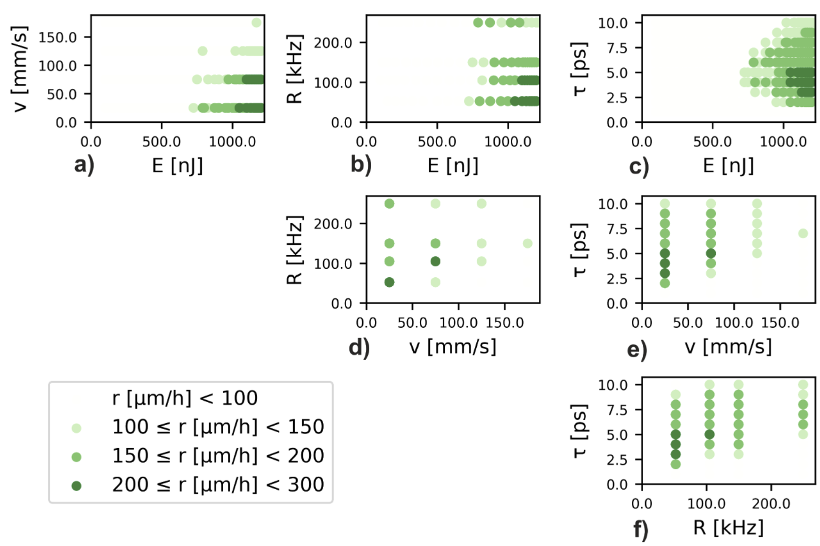

Fig. 4. Etch rate r classification of through holes in borosilicate glass BF33 as a function of pulse energy E, writing speed v, repetition rate R and pulse duration τ. The graphs show the maximum obtained etch rate class in the analyzed parameter space.

Figure 4(a) shows the dependence of the etch rate as a function of pulse energy and writing speed. A writing speed of 75 mm/s requires pulse energies of more than 1100 nJ. For writing speeds of 25 mm/s the pulse energies have to be greater than 1000 nJ. From the graph in Fig. 4(d) it can be concluded that the highest etch rates can be obtained using a repetition rate of 52 kHz or 105 kHz and a writing speed of 25 mm/s or 75 mm/s. In a next step the etch rate dependence on the pulse duration and repetition rate is analyzed in Fig. 4(f). Here the etch rate is plotted as a

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function of the pulse duration and the repetition rate. This graph again contains all the results of the parameter study but again only the results with the highest etch rate for different pulse energies and writing speeds are shown. For a repetition rate of 52 kHz the highest etch rates could be observed for pulse durations of 3, 4 or 5 ps. Repetition rates of 105 kHz show the best etch rates for 5 ps pulses.

The following set of processing parameters proved to be most promising for an optimal etch rate:

- Writing speed: 25, 75 mm/s
- Repetition rate: 52, 105 kHz
- Pulse duration: 3, 4, 5 ps

For a competitive production, lead times and costs per device need to be reduced. Therefore, a fast writing speed is an essential parameter for the manufacturing of three-dimensional objects. In consequence, the laser parameter combination A = (105 kHz; 5 ps; 75 mm/s) is further investigated in the following etching rate and selectivity tests.

3.2. Etch rate and selectivity of laser-modified borosilicate glass

In the previous study (Section 3.1) it became clear that the highest etch rates combined with high writing speeds can be achieved for the parameter set A with pulse energies > 1000 nJ, a pulse duration of 5 ps, a repetition rate of 105 kHz and a writing speed of 75 mm/s. It must be considered that the economic efficiency of the selective laser etching process depends mainly on the writing speed, as this correlates directly with the production time. For this reason, writing speeds of 65, 70, 80 and 85 mm/s, centered around 75 mm/s were analyzed in additional experiments to investigate the dependence of the writing speed more precisely. For each writing speed, an extended range of pulse energies was examined to study the modification thresholds observed in the previous study in more detail (Section 3.1).

In the next set of tests, the etching selectivity was investigated using channel structures in the glass volume. The channels were manufactured by writing lines below the surface with subsequent wet chemical etching for about 4 h. The etch rate was then calculated by measuring the different lengths of the etched channels. Figure 5 shows a microscope image of the etched channels for different pulse energies. The longest channels correlated with an etch rate of 320 μm/h.

For each parameter set, two lines – one in forward and one in reverse direction - were written with the ultrashort pulse laser. To improve the statistical significance of the results each parameter set was repeated five times on the sample. After material modification by laser writing, the substrate with a size of 4 inches was cleaved at two positions. The result is a sample with two cleaved edges (see Fig. 5 top). The sample was etched as described above from both sides. The resulting etched channels were measured and the corresponding etch rates r_1 of the modified material were calculated.

For selectivity determination, the etch rate r_0 of the unmodified material had to be measured in addition. This was done by etching a non-laser treated substrate for about 24 h and measuring the thickness change Δd_{sub}. The etch rate of the unmodified BF33 was found to be 0.59 μm/h. For each parameter set the selectivity was calculated as the average from 10 lines/channels (5 channels per cleaved edge for a certain writing direction) and the results were plotted as a function of the applied pulse energy (Fig. 6). Selectivities up to 540 were observed for a repetition rate of 105 kHz.

Figure 6 shows the selectivity for BF33 for a repetition rate of 105 kHz as a function of pulse energy. For each pulse energy the average and the standard deviation of 10 measurements are shown. It can be observed that the selectivity for each writing speed in a narrow pulse energy

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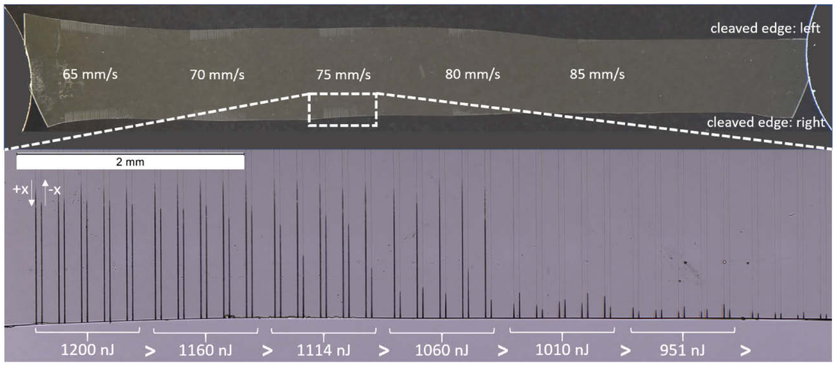

Fig. 5. Overview picture of the cleaved sample and polarization contrast microscope image of etched line pairs in borosilicate glass BF33 written with the following parameter set: writing speed: 75 mm/s; pulse duration: 5 ps; repetition rate: 105 kHz. The etched lines are visible as thick dark gray lines on top of the lines written by the laser (light gray). One line of a respective line pair is written in forward direction (+x) the other line in reverse direction ($-x$).

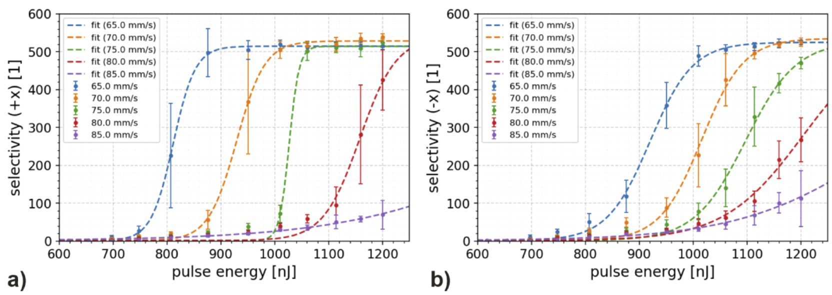

Fig. 6. Etch rate selectivity of laser-modified and unmodified borosilicate glass as a function of pulse energy at a repetition rate of 105 kHz for a pulse duration of 5 ps. The average selectivity and standard deviation for each pulse energy is shown. In addition, a selectivity model based on a logistical function was fitted into the data set to visualize the pulse energy threshold of the different writing speeds and the difference between the a) forward and b) backward written lines.

range increases rapidly from low selectivity to high selectivity as the pulse energy is increased. The plot describing the selectivity dependence on pulse energy has the shape of an "S"-shaped curve. Furthermore, the data sets show that an increase in writing speed requires a higher pulse energy to achieve a high selectivity. Therefore, a selectivity model based on a logistic function is applied to the data sets to determine the threshold value of pulse energy needed to achieve high selectivity.

The applied selectivity model has the form $S = (S_{max} - 1)/(1 + e^{-k(E-E_{th})}) + 1$. S_{max} is the maximum selectivity, k the growth factor of the edge and E_{th} the edge position i.e. pulse energy threshold. This mathematical model was fitted into the data set to visualize the pulse energy threshold for different writing speeds and the difference between the forward (Fig. 6(a)) and backward (Fig. 6(b)) written lines. The dashed lines in the Fig. 6 are showing the fitted models.

The analysis of the adapted model shows that an increase in writing speed shifts the modification threshold to higher pulse energies. Furthermore, high pulse energies correlate with high selectivities. By comparing the highest selectivities (S_{max}) of the different writing speeds, it can be concluded that no speed dependence is observable.

Matsuo et al. analyzed the same material as in this study with a higher numerical aperture of 1.35. They found an energy threshold of about 200 nJ [8]. The measured energy thresholds in the present study is higher by a factor of 4 to 5. Most likely this results from the different numerical apertures. In Fused Silica, an energy threshold of about 150 nJ was found by Hermans et al. by using a higher repetition rate of 750 kHz and a pulse length of 1 ps [12]. In their study a maximum etch rate of 290 μm/h was found, which is comparable with the maximum etch rate in the present study of 320 μm/h. In alumino-borosilicate glass experimental results were presented by Crespi et al. by using a higher NA of 0.6, a high repetition rate of 1 MHz and a shorter pulse length of 300 fs [5]. They found an energy threshold of about 500 nJ and an etch rate of 17 μm/h. Unfortunately, all these results are not directly comparable with the results presented here. In comparison to the cited papers, we used a lower repetition rate of 105 kHz and a higher pulse duration of 5 ps.

The microscope image in Fig. 5 shows that the length of the line pairs written in forward and backward direction is not always the same. This becomes obvious when comparing the selectivity curves of Fig. 5(a) and Fig. 5(b). Anisotropic material modifications in isotropic materials were also observed by other authors [14,15]. This behavior is related to the asymmetry of pulsed laser beams with an inclined intensity front [14,16].

Figure 7 shows the adjusted pulse energy thresholds with their 95% confidence intervals for the forward and backward direction plotted against the writing speed. The differences between forward and backward direction are significantly higher than the confidence interval. Furthermore, it can be observed that the effect becomes smaller as the pulse energy becomes higher.

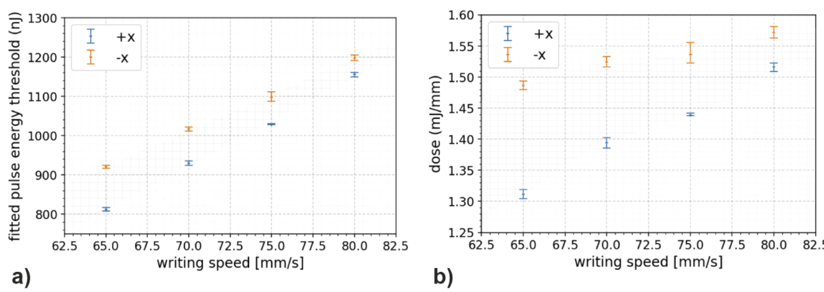

Fig. 7. Pulse energy threshold a) and dose threshold b) of the selectivity as a function of writing speed, fitted by a model based on a logistical function. The graphs show the energy threshold and dose threshold for each writing speed together with the corresponding 95% confidence interval.

Considering the repetition rate and the writing speed, the applied dose (energy per length) can be determined from the pulse energy threshold. For linear processes the dose threshold is expected to be independent of the writing speed. However, our results show a dependence. This could be a consequence of the geometric distance between two successive pulses. The pulse spacing becomes larger if the writing speed is increased due to the constant pulse repetition rate of 105 kHz. A larger pulse spacing affects the heat accumulation, which could be a reason why a higher dose is required for higher writing speeds.

3.3. Three-dimensional shapes in borosilicate glass

To demonstrate the capabilities of the presented manufacturing process for 3D glass devices, hemispheres, cones, V-grooves and stairs were produced in a 500 μm thick borosilicate substrate by using the optimum parameter set A (pulse repetition rate of 105 kHz, writing speed of 75 mm/s and a pulse length of 5 ps). The laser power was adjusted according to the writing depth as described in section 2.3. The minimum laser power was selected to be 96% (1100 nJ) at the

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correction depth of 1.1 mm. The linear power correction in z-direction was set to 3.9 %/mm (50 nJ/mm). Additionally, the same geometry was produced in Fused Silica. In Fig. 8 scanning electron microscope images of different 3D glass devices in Fused Silica are shown.

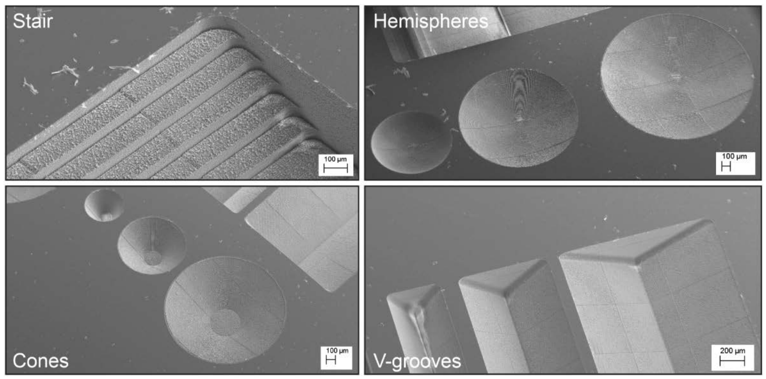

Fig. 8. Scanning electron microscope images of selective laser etched 3D test structures in Fused Silica

The different structures were characterized by focus variation (Alicona InfiniteFocus G5). In Fig. 9 the depth map of the structure in borosilicate BF33 is shown. By using this dataset, the levels of the stair steps, the radius of the hemispheres, the aperture angles of the cones and the opening angles of the V-grooves were analyzed.

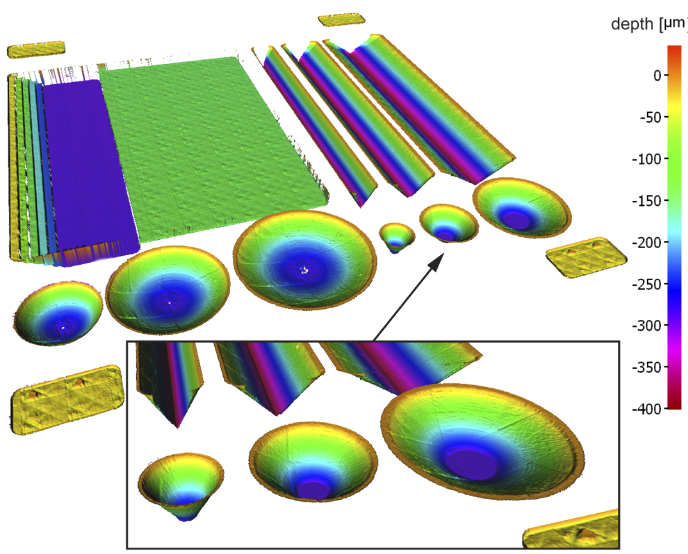

Fig. 9. Depth profile of the selective laser etched test structure in BF33. The depth map was measured using focus variation.

In Table 2 the measured geometrical properties of the etched 3D shapes in BF33 and Fused Silica are listed. One important tolerance for manufacturing is the precision in z direction. By comparing the results of the distances between substrate plane and the stair steps (levels) it can been concluded that the manufacturing deviation in z direction is in the range of 1%. Furthermore, only a small difference can be observed between the BF33 and Fused Silica sample. Commonly used geometries in packaging and optical applications are spheres and hemispheres respectively.

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The measured radii of the manufactured hemispheres in BF33 with a design radius of 500, 1000 and 1500 μm are larger than designed by a value of 13 to 30 μm. The radii of the hemispheres in Fused Silica are more precise with a deviation of 1 to 4 μm. For packaging applications, cones or V-grooves are often used to mount components like fibers or balls. Essential for these components is the opening angle, which affects the positioning accuracy. A look at Table 2 shows that the angles in borosilicate glass have a deviation of less than 1.3%.

Table 2. Geometrical properties of 3D shapes in the borosilicate glass BF33 and Fused Silica (FS) measured by focus variation

feature	property	unit	design	BF33	Δ_{BF33}	FS	Δ_{FS}
	level of step 1	μm	−50	−50	0	−50	0
	level of step 2	μm	−100	−101	1	−101	1
stair	level of step 3	μm	−150	−151	1	−153	3
	level of step 4	μm	−200	−201	1	−202	2
	level of step 5	μm	−250	−252	2	−252	2
	radius 1	μm	500	513	13	504	4
hemispheres	radius 2	μm	1000	1024	24	1001	1
	radius 3	μm	1500	1530	30	1502	2
	angle 1	°	60	59.86	−0.14	58.40	−1.60
cones	angle 2	°	90	91.22	1.22	88.50	−1.50
	angle 3	°	120	120.58	0.58	118.70	−1.30
	V-groove angle 1	°	60	59.52	−0.48	58.23	−1.77
V-grooves	V-groove angle 2	°	90	90.18	0.18	87.86	−2.14
	V-groove angle 3	°	120	119.90	−0.10	123.15	3.15

In addition to the 3D shapes, test areas of about 2.5 x 4 mm^2 were implemented to measure the flatness and roughness of the etched surfaces. The measurements show a rms-roughness in borosilicate glass of 1.2 μm, if a 0.8 μm gaussian filter is applied. This value is comparable to the results obtained in Fused Silica of 0.9 μm.

4. Conclusion

The result of the presented parameter study is a very promising set of process parameters for selective laser etching of borosilicate glass using an objective lens with numerical aperture of 0.4.

Wang et al. reported in 2019 a selective laser etching process for Fused Silica by using a numerical aperture of 0.14 and a pulse width of about 10 ps [17]. In our study we also observed that the tuning of the pulse length into the picosecond range is an essential parameter for borosilicate glass to increase the selectivity if a lower NA objective lens is used. Matsuo et al. reported in 2009 a maximum etching rate in the borosilicate glass Pyrex of 240 μm/h by using an objective lens with a numerical aperture of 1.35 [8]. In the present study etching rates in BF33 of about 320 μm/h could be achieved. Furthermore, a selectivity greater 540 is achievable by using writing speeds of up to 80 mm/s. In comparison, the selectivities of Fused Silica are two to three times higher [12], which is mainly due to the lower etching rate of the unmodified Fused Silica material. Non-modified Fused Silica has an etch rate r_0 of about 0.2 μm/h compared to non-modified BF33 with an r_0 of about 0.6 μm/h.

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References

1. K. Sugioka and Y. Cheng, *Femtosecond Laser 3D Micromachining for Microfluidic and Optofluidic Applications*, SpringerBriefs in Applied Sciences and Technology (Springer, 2014).
2. M. Lancry, F. Zimmerman, R. Desmarchelier, J. Tian, F. Brisset, S. Nolte, and B. Poumellec, "Nanogratings formation in multicomponent silicate glasses," Appl. Phys. B **122**(3), 66 (2016).
3. M. Masuda, K. Sugioka, Y. Cheng, N. Aoki, M. Kawachi, K. Shihoyama, K. Toyoda, and K. Midorikawa, "3D microfabrication in photosensitive glass by femtosecond laser," in *Conference Proceeding LAMP 2002*, I. Miyamoto, K. F. Kobayashi, K. Sugioka, R. Poprawe, and H. Helvajian, eds. (SPIE, 2002), SPIE Proceedings, p. 576.
4. Y. Bellouard, A. Said, M. Dugan, and P. Bado, "Fabrication of high-aspect ratio, micro-fluidic channels and tunnels using femtosecond laser pulses and chemical etching," Opt. Express **12**(10), 2120 (2004).
5. A. Crespi, R. Osellame, and F. Bragheri, "Femtosecond-laser-written optofluidics in alumino-borosilicate glass," Opt. Mater.: X **4**, 100042 (2019).
6. C. Hnatovsky, R. S. Taylor, E. Simova, P. P. Rajeev, D. M. Rayner, V. R. Bhardwaj, and P. B. Corkum, "Fabrication of microchannels in glass using focused femtosecond laser radiation and selective chemical etching," Appl. Phys. A **84**(1-2), 47–61 (2006).
7. S. Juodkazis, "Forming tiny 3D structures for micro- and nanofluidics," SPIE Newsroom (19 March 2007).
8. S. Matsuo, H. Sumi, S. Kiyama, T. Tomita, and S. Hashimoto, "Femtosecond laser-assisted etching of pyrex glass with aqueous solution of koh," Appl. Surf. Sci. **255**(24), 9758–9760 (2009).
9. C. Hnatovsky, R. S. Taylor, E. Simova, V. R. Bhardwaj, D. M. Rayner, and P. B. Corkum, "Polarization-selective etching in femtosecond laser-assisted microfluidic channel fabrication in fused silica," Opt. Lett. **30**(14), 1867–1869 (2005).
10. S. Ho, P. R. Herman, and J. S. Aitchison, "Single- and multi-scan femtosecond laser writing for selective chemical etching of cross section patternable glass micro-channels," Appl. Phys. A **106**(1), 5–13 (2012).
11. C. Ross, D. G. MacLachlan, D. Choudhury, and R. R. Thomson, "Towards optical quality micro-optic fabrication by direct laser writing and chemical etching," in *Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications XVII*, A. Heisterkamp, P. R. Herman, M. Meunier, and R. Osellame, eds. (SPIE2017), SPIE Proceedings, p. 100940V.
12. M. Hermans, "Selective, laser-induced etching of fused silica at high scan-speeds using koh," J. Laser Micro/Nanoeng. **9**(2), 126–131 (2014).
13. J. Gottmann, M. Hermans, N. Repiev, and J. Ortmann, "Selective laser-induced etching of 3D precision quartz glass components for microfluidic applications—up-scaling of complexity and speed," Micromachines **8**(4), 110 (2017).
14. Y. Dai, J. Ye, M. Gong, X. Ye, X. Yan, G. Ma, and J. Qiu, "Forced rotation of nanograting in glass by pulse-front tilted femtosecond laser direct writing," Opt. Express **22**(23), 28500–28505 (2014).
15. P. G. Kazansky, W. Yang, E. Bricchi, J. Bovatsek, A. Arai, Y. Shimotsuma, K. Miura, and K. Hirao, "'Quill' writing with ultrashort light pulses in transparent materials," Appl. Phys. Lett. **90**(15), 151120 (2007).
16. P. G. Kazansky, Y. Shimotsuma, M. Sakakura, M. Beresna, M. Gecevičius, Y. Svirko, S. Akturk, J. Qiu, K. Miura, and K. Hirao, "Photosensitivity control of an isotropic medium through polarization of light pulses with tilted intensity front," Opt. Express **19**(21), 20657–20664 (2011).
17. P. Wang, W. Chu, W. Li, Y. Tan, F. Liu, M. Wang, J. Qi, J. Lin, F. Zhang, Z. Wang, and Y. Cheng, "Three-dimensional laser printing of macro-scale glass objects at a micro-scale resolution," Micromachines **10**(9), 565 (2019).