Selective, Laser-Induced Etching of Fused Silica at High Scan-Speeds Using KOH

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Selective, laser-induced etching (SLE) is a process which offers the possibility of machining hollow volumes into transparent materials with a huge freedom of geometry in 3D. Every 3D structure consists of single lines of laser-induced modifications. The knowledge of selectivity for etching of these single lines of modification is crucial to identify stable process windows for the machining of completely integrated, complex 3D structures. The selectivity of laser-induced etching of single line modifications is investigated in this study for a variation of repetition rate, pulse duration, pulse energy and feed rate for etching with KOH.

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1. Introduction

Focusing ultrashort pulsed laser radiation with a NA>0.2 leads to focal intensities in the order of $I > 10^{12}$ W/cm² at pulse energies in the order of hundreds of nanojoule. At these intensities non-linear photoionization occurs in the vicinity of the focus when it is positioned within the volume of a dielectric transparent to the wavelength of the laser radiation. The generation of free electrons by non-linear absorption enables further absorption of radiation by Bremsstrahlung absorption leading to avalanche-like increase of the number of free electrons [1]. The energy of the electron system excited like that is partially transferred to the atoms via electron-phonon coupling and leads to heating of the material up to temperature differences in the order of several 1000 K depending on the material and parameters of irradiation [2]. Moving the focal spot with feed rates >100 mm/s at pulse repetition rates >500 kHz through the material leads to rapid quenching of the material and thus permanently freezing in an high temperature, high pressure state of the material. By moving the focal spot through the material arbitrarily in 3D, a continuous line-shaped modification is formed. In case the modified material has somewhere contact to the outer side of the sample, putting the sample in a suitable wet etching agent as a second process step results in the solution of the modified material at a higher rate than the non-modified material. The ratio between the etching rates of modified and non-modified material is called selectivity and is equivalent to the possible maximum aspect ratio of machinable structures. This two-step process of modifying material with laser radiation and removing mainly the modified material with a subsequent step of wet etching is called *Selective Laser-induced Etching* (*SLE*). This process offers unique features for machining arbitrary hollow volumes within transparent materials like crystals or glasses with precisions in the order of 1 µm by stacking single line-shaped modifications to get the desired shape.

Marcinkevičius et al.was the first group to report about using *SLE* for micro fabrication of 3D microfluidic channels in fused silica with HF as etching agent [3]. For 2.5% HF etching selectivities up to ~100 and an etching rate of 70µm/h at a feed rate of 30 mm/s can be achieved [4].

For selective etching in fused silica HF can be substituted as etching agent with KOH with the advantage of a reduced harmfulness to the human body and a constant selectivity in dependence of the length of the evolving micro channel achieving selectivities up to 350 [5]. This is why the authors of the study at hand focused their investigations on etching the laser-induced line modifications with KOH.

Applications for *SLE* range from the simple creation of precise cuts to the fabrication of complete already-mounted micro-mechanical systems and microfluidic elements [6-10] (Figure **1**). Speeding up the process is necessary for establishing *SLE* as an economically worthwhile production

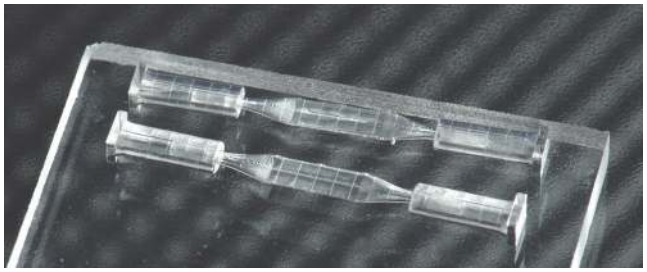

Figure 1 Micro-fluidic chip with built-in side connectors for attachment of flexible tube for automated cell diagnostics fabricated inside fused silica by SLE; length 15 mm, height 2 mm

process. This can be achieved by the development of faster scanning systems for spot sizes in the micrometer range and has already been reported up to feed rates in the order of 10 m/s within fused silica [11]. In order to overcome process limitations like crack formation it is crucial to have knowledge about the dependency of etching selectivity from pulse repetition rate, pulse energy and feed rate for single line-shaped modifications before stacking singe lines to complex 3D structures.

While for feed rates in the order of 1 mm/s the aforementioned dependencies have been reported for fused silica using KOH as etching agent, this data is not available for feed rates up to 200 mm/s. By the results of this work this gap is intended to be closed.

2. Experimental Setup & Procedure

Lines of laser induced modifications are inscribed 200 µm beneath the surface of flat test pieces of fused silica (Suprasil1, Heraeus GmbH; Hanau, Germany). The laser source used for the experiments is a FCPA laser (Satsuma, Amplitude Systèmes; Bordeaux, France) providing pulsed laser radiation at a wavelength of 1030 nm with pulse durations ranging from 300 to 3000 fs with a maximum pulse energy of 20 µJ at 500 kHz and repetition rates ranging from 0 to 17 MHz. Laser radiation is focused by a 20x microscope objective with a numerical aperture of 0.45 (LCPLAN N 20x/0.45 IR, Olympus Europa GmbH; Hamburg, Germany) equipped with a collar for correction of spherical aberrations. The spherical aberrations of a non-collimated beam at a plane surface are compensated according to the depth of modification. Measurement of the focal spot diameter $2w_0$ with a 40x/0.8 microscope objective in combination with a linearized CMOS camera (BladeCam XHR, Data Ray Inc.; Bellavista, USA) yields $2w_0$=2.2 µm with a resolution of the system better than 1.7µm (Figure **2**).

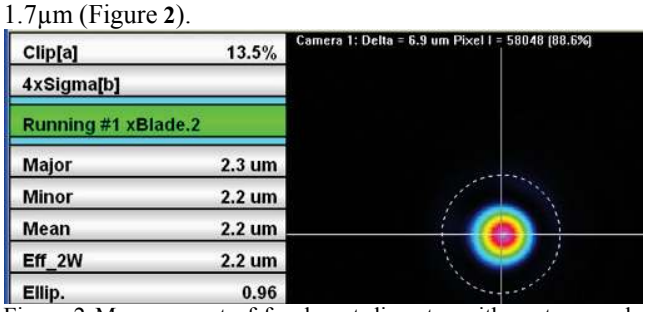

Figure 2 Measurement of focal spot diameter with custom made setup; resolution <1.7µm

Polarization of the laser radiation is linear and chosen to be perpendicular to the feed rate vector due to the fact that this orientation of polarization yields the highest selectivities [5,6]. The fused silica samples are mounted and aligned on a xy-system of air bearing stages (ABL 10100 and ABL 20030, Aerotech Inc.; Pittsburgh, USA). For irradiation the parameters pulse energy E_p, repetition rate f_{rep}, feed rate v_{xy}, and pulse duration t_p are varied according to table 1. Pulse energy is measured below the microscope objective without sample. Modifications are inscribed 3 times back and forth respectively resulting in 6 lines of modification for each parameter combination with a distance of 100 µm between each line.

Table 1 Parameter variation for irradiation

Parameter	Variation	Steps/Value
Pulse energy E_p	100-1000 nJ	100 nJ
Repetition rate f_{rep}	250-4000 kHz	250 kHz
Feed rate v_{xy}	50-200 mm/s	50 mm/s
Pulse duration t_p	300-1000 fs	100 fs

After irradiation and modification the samples are grinded in the plane spanned from the feed rate vector during line modification in order to make sure that the modified material has contact to the outer side of the sample.

The samples are placed into a wet-etching bath of potassium hydroxide (KOH) with a concentration of 8 mol/l at a temperature of 85 °C for 6 hours.

After wet-etching the developed in-volume microchannels are being investigated by transmitted light microscopy with polarization contrast, the length of the channel l is measured and subsequently the rate of selective etching r_s is calculated. The unetched modification appears bright due to birefringence resulting from nanogratings (NG) and/or stress induced birefringence. The etched micro channel appears black (Figure **3**) with no birefringence left behind.

In order to determine the selectivity S of the etching process, the ratio of etch rates is calculated according to

$$S = \frac{r_s + r_0}{r_0} \quad (1)$$

Where r_0 denotes the etch rate of non-modified fused silica which is measured to be 0.21±0.015 µm/h at a temperature of 85 °C and a concentration of 8 mol/l being in good agreement with an etching rate of 0.25 µm/h at 80 °C and 10 mol/l as reported in [5].

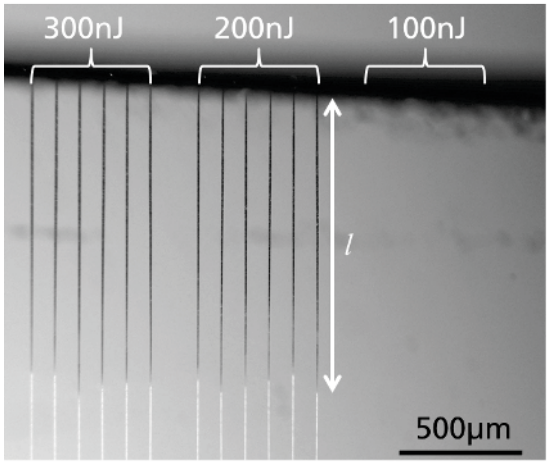

Figure 3 Micro graph with polarization contrast of modified and etched sample, micro channels with length l appear black, unetched modification appear bright due to birefringence; f_{rep}=750kHz, t_p=800 fs, v_{xy}=100 mm/s (top view)

3. Results & Discussion

The general dependencies of selectivity on the parameters varied for the study at hand are discussed and are shown exemplarily for chosen parameters. The largest selectivity found in this study is $S \sim 1400$ together with a selective etching rate of $r_s \sim 290$ µm/h.
For all the parameters investigated the selectivity depends similarly on the pulse energy applied. For a pulse energy E_p=100 nJ no visible line of modification can be detected and no micro channels have developed after etching (Figure 3). For 200 nJ a visible modification along with an etched micro channel can be observed corresponding to a threshold fluence for modification of ~5J/cm².
Two process windows for selective etching are found. The highest selectivity for micro channels is observed along with straight and smooth sidewalls pulse energies between 200 and 500 nJ within the range of all repetition rates, feed rates and pulse durations investigated. For pulse durations t_p>400 fs the maximum selectivity does not depend on pulse duration in terms of measurement accuracy (Figure 4) within this first process window.

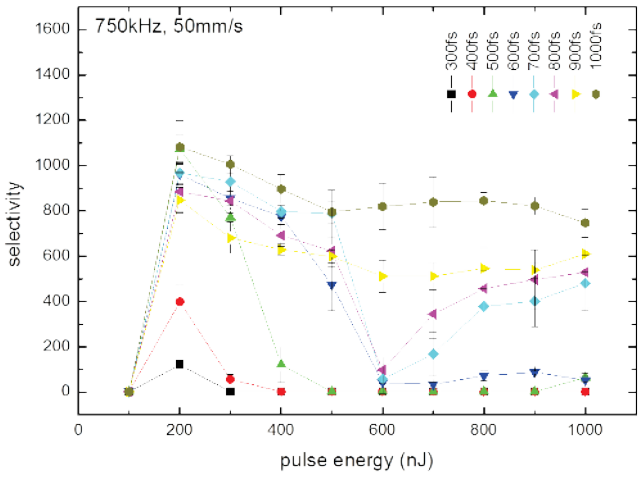

Figure 4 Selectivity vs. pulse energy; f_{rep}=750 kHz, 50 mm/s

The second process window for selective etching is found for pulse energies $E_p > 700$ nJ. The micro channels feature irregular sidewalls presumably originating from micro cracks widened by the etching process (Figure 5 inlay left). For pulse durations $t_p < 900$ fs selectivity between the two process windows drops. Furthermore for $t_p < 500$ fs and $v_{xy} < 100$ mm/s the second process window does not exist. One difference between those two process windows is revealed by a more detailed view on the unetched modifications. The structure of the line modification (Figure 6) for 600 nJ pulse energy features irregularities larger than 2 µm which are formed by periodically appearing bubbles or maybe voids surrounded by an in transmission light microscopy brighter appearing material. This brighter appearing material probably consists of molten and resolidified material (Figure 6).

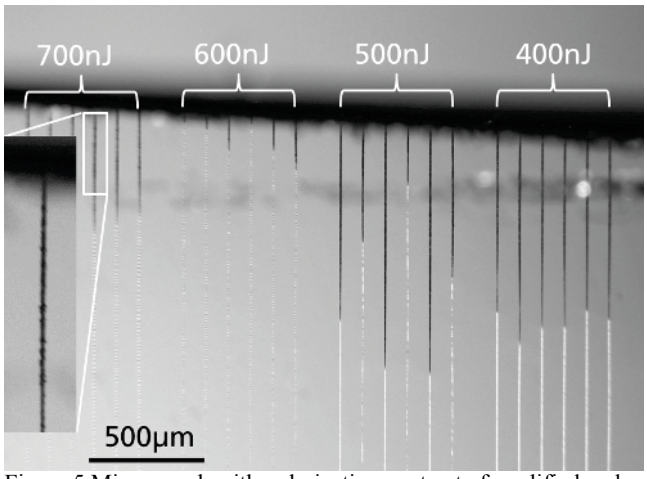

Figure 5 Micro graph with polarization contrast of modified and etched sample, micro channels appear black, unetched modification appear bright due to birefringence; for a pulse energy E_p=600nJ a decrease in selectivity is observable; f_{rep}=750kHz, t_p=800 fs, v_{xy}=50 mm/s (top view)

For E_p=500 nJ these irregularities can be observed only for one direction of the feed rate indicating a defined threshold for the development of the irregularities during modification (Figure 6). A different energy deposition for the forth and back direction could be attributed to a quill writing effect resulting from a tilted pulse front as reported in [12].

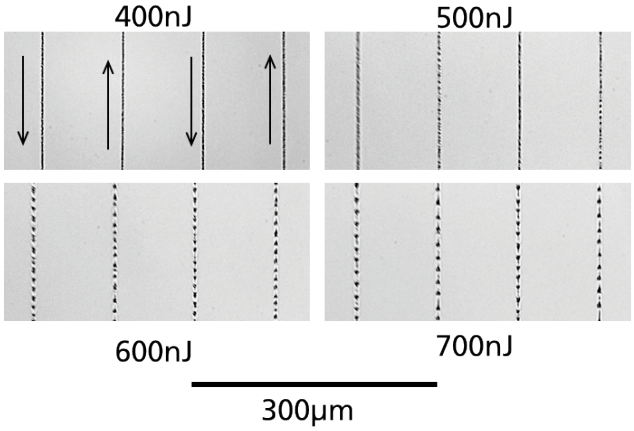

Figure 6 Micro graph in transmitted light microscopy of in-volume modification at different pulse energies applied (top view); back and forth direction is indicated by arrows; f_{rep}=750kHz, t_p=800 fs, v_{xy}=50 mm/s

Furthermore appearing irregularities and probably molten and resolidified material coincide with a lower selectivity observed after wet-etching (Figure 5).
For repetition rates $f_{rep} > 1000$ kHz no selective etching is observed at all. The line modifications within this regime feature molten material periodically interrupted by bubbles as reported in [14].

At higher feed rates the first process window for pulse durations $t_p < 600$ fs is larger (Figure 7), i.e. for a wider range of pulse energies a selectivity $S > 800$ is observed. The second process window exists for all pulse durations investigated, still separated by a dip in selectivity from the first process window for $t_p < 600$ fs. Corbari et al. also found a dip in selectivity at interim fluences for femtosecond pulses

while for picosecond pulses they observed an almost constant selectivity [13].

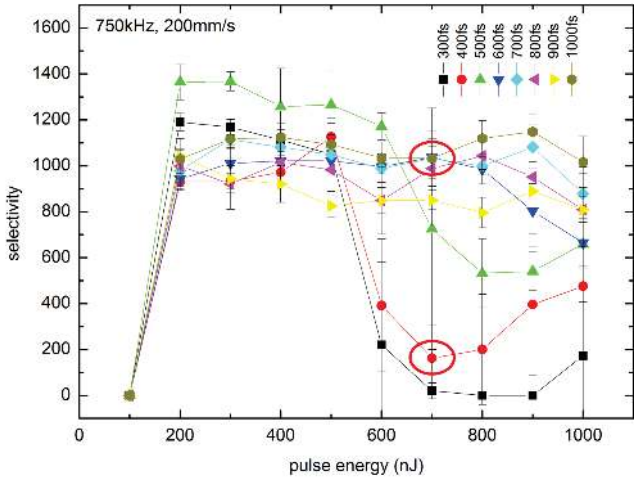

Figure 7 Selectivity vs. pulse energy; f_{rep}=750 kHz, 200 mm/s

Comparison of two unetched line modifications at different pulse durations one exhibiting the dip in selectivity one not (red circles in Figure 7) by means of polarization contrast microscopy reveals differences in terms of birefringence. For a pulse duration of t_p = 400 fs the observed birefringence does not depend on the angle between line modification and the polarization of the light for illumination (Figure 8 top row) and is comparably weak. For a pulse duration of t_p = 1 ps the birefringence exhibits an anisotropy in relation to the orientation of the polarization of the illumination light. Rotating the sample by an angle of 45° leads to a clear drop in intensity of the observed light (Figure 8 bottom row). Rotating the sample further by an angle of 45° the maximum intensity is found again. Furthermore the observed birefringence is stronger than for t_p = 400 fs.

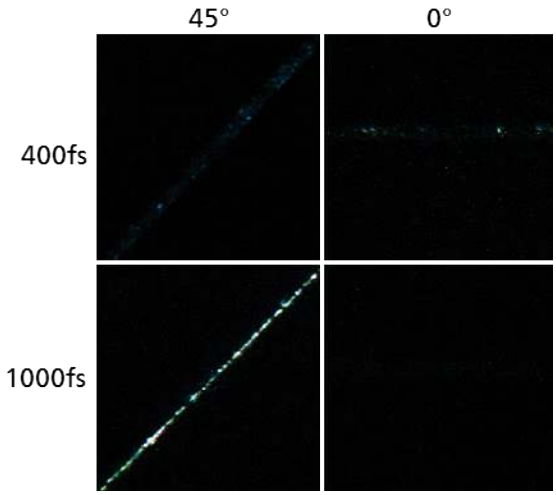

Figure 8 Micro graph of unetched line modifications for two different pulse durations (top: 400 fs, bottom: 1 ps) in polarization contrast at two different angles in relation to the orientation of the first polarizer, micro graphs taken under same exposure time and ISO number; E_p = 700 nJ, f_{rep} = 750 kHz, v_{xy} = 200 mm/s

According to [15] and [16] the anisotropy in birefringence is attributed to the formation of NG's within the line modification. This leads to the conclusion that at otherwise equal parameters for irradiation the formation of NG's is found for t_p = 1000 fs whereas for t_p = 400 fs it is not. This implies that the classification introduced by Hnatovsky et al. in [17] has to be extended and modified for pulse durations around 1 ps. There is a larger range of pulse energies where NG's are found for 1 ps than for 400 fs (called regime 2 in [17]). The observed higher selective etching rate for a line modification exhibiting NG's furthermore supports the idea that the formation of NG's are at least one driving force for selective etching as expressed in [18]. The temporal formation dynamics of NG's and the possible decomposition of SiO_2 into SiO and O^+ as suggested by Canning et al. in [19] has to be investigated more intensely in order to explain the presence of NG's for a pulse duration of 1 ps while irradiation with 400 fs does not lead to the formation of NG's.

In order to discuss the differences in selectivity found for t_p = 1 ps and t_p = 400 fs in dependence of all other parameters varied the results are visualized in terms of the net fluence F_{net} as proposed in [13]. There the net fluence is defined as the accumulated deposited energy per area. It can be calculated as the product of the number of pulses per spot N_{eff} and the fluence F:

$$F_{net} = N_{eff} \cdot F = \frac{2w_0 \cdot f_{rep}}{v_{xy}} \cdot \frac{E_p}{\pi w_0^2} \qquad (2)$$

For a pulse duration of t_p = 400 fs and f_{rep} = 250-750 kHz a process window exists for net fluences up to ~100 - 150 J/cm² (Figure 9).

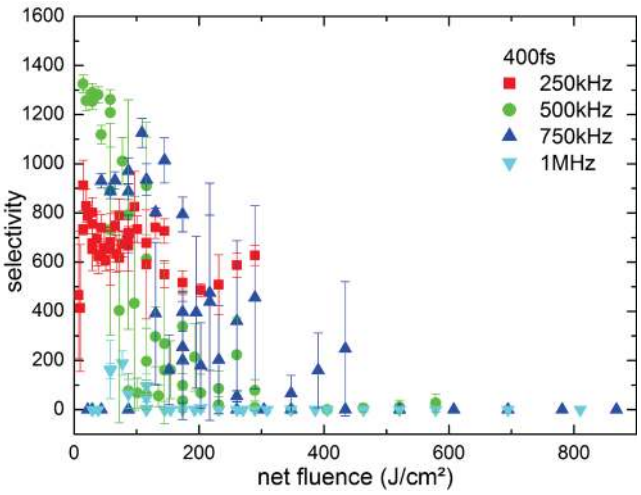

Figure 9 Selectivity vs. net fluence F_{net} for the variation of v_{xy}, f_{rep} and E_p investigated at a fixed pulse duration of t_p = 400 fs.

Higher net fluences lead to formation of channels featuring irregularities at their sidewalls as seen in the inset of Figure 5 also indicated by larger error bars in Figure 9. The maximum selectivity depends on the pulse repetition rate and is highest for f_{rep} = 500 kHz with ~1300 and lowest for f_{rep} = 250 kHz with ~700. No process window is found for f_{rep} = 1 MHz.
For a pulse duration of t_p = 1 ps and f_{rep} = 250-750 kHz a process window exists for net fluences up to ~800 J/cm² (Figure 10). Especially for 750 kHz an almost constant se-

lectivity is observed over a broad range of net fluences applied.
For f_{rep} = 1 MHz a process window exists, but is smaller than for the other repetition rates investigated. For net fluences F_{net}>200 J/cm² heat accumulation starts to play a role.

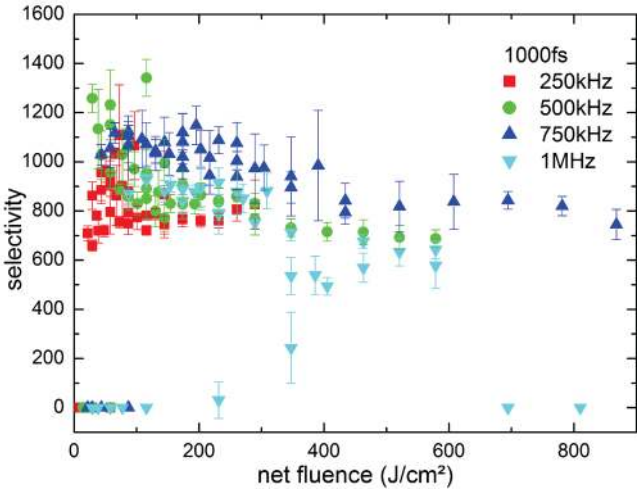

Figure 10 Selectivity vs. net fluence F_{net} for the variation of v_{xy}, f_{rep} and E_p investigated at a fixed pulse duration of t_p = 1 ps.

As already stated above several groups have reported that the NG's are on nano-scale periodically alternating layers of pristine SiO_2 and SiO_{2-x} with nano-sized bubbles of O_2[19]. The selective etching of fused silica in a solution of KOH can then be attributed to the chemical reaction of OH^- ions with the silicon-richer material in the NG's [5]. This gives rise to comparison of the selective etching rates in a solution of KOH found in the present study with those from c-silicon and thermally grown SiO_2 reported in literature [20]. The maximum etch rate found within the range of parameters applied for investigation is 290±7 µm/h which is about a factor of 2-3 higher than the etch rate reported for c-silicon in the <110> and in the <100> plane respectively (Figure 11).

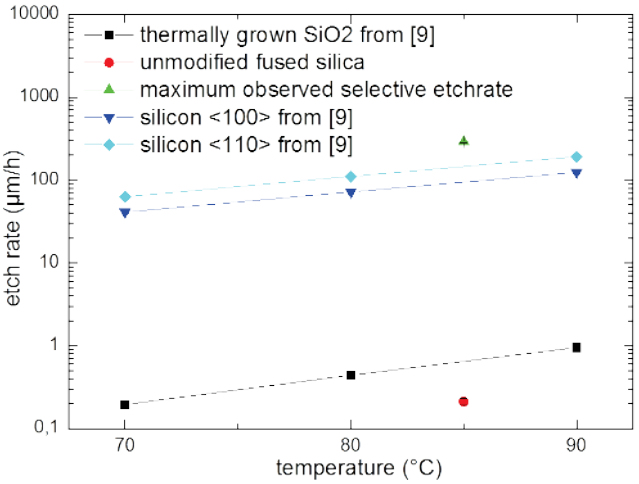

Figure 11 Etch rate vs. temperature for comparison of etch rates in KOH of thermally grown SiO_2, unmodified fused silica as used in the present study, silicon for different orientations and the maximum observed etch rate of a modified line structure

The etch rate of thermally grown SiO_2 reported in the literature [20] is ~3 times higher than the etch rate observed for unmodified fused silica in this study.
The deviation of the etch rates between laser-modified fused silica and c-silicon can be explained by the speculation that, in case there is silicon-rich material within the NG's, it could be in an amorphous state which presumably shows higher etch rates towards KOH than the c-silicon. To the best knowledge of the authors the etch rate of amorphous silicon towards KOH hasn't been reported yet. Furthermore the nanoporous material offers a higher surface for the chemical reaction so that a higher rate of selective etching can be attributed to this.

4. Conclusion

In the present study the dependence of laser-induced selective etching on pulse duration, feed rate, repetition rate and pulse energy for a numerical aperture of NA=0.45 is investigated. Process windows for machining fused silica with SLE are identified with maximum selectivities up to ~1400 and selective etching rates up to ~290 µm/h. By the best knowledge of the authors this is the highest observed selectivity and selective etching rate for the SLE process in fused silica. The selective etching rate with KOH is even higher than for etching with ~2% HF reported in [5,6,18]. Irradiation with pulse durations t_p<600 fs lead to a varying width of process window. Wider process windows can be found for t_p>800 fs attributed to a more stable formation of NG's at these pulse durations.
The SLE process is scalable to higher feed rates without sacrificing selectivity within the range of parameters used for irradiation.
The largest selective etch rate found is significantly higher than the one of crystalline silicon under the same etching conditions reported in the literature.

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