# Sub-surface channels in sapphire made by ultraviolet picosecond laser irradiation and selective etching

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**Abstract:** We demonstrate the realization of sub-surface channels in sapphire prepared by ultraviolet picosecond laser irradiation and subsequent selective wet etching. By optimizing the pulse energy and the separation between individual laser pulses, an optimization of channel length can be achieved with an aspect ratio as high as 3200. Due to strong variation in channel length, further investigation was done to improve the reproducibility. By multiple irradiations the standard deviation of the channel length could be reduced to 2.2%. The achieved channel length together with the high reproducibility and the use of a commercial picosecond laser system makes the process attractive for industrial application.



**OCIS codes:** (220.4000) Microstructure fabrication; (220.4610) Optical fabrication; (260.7190) Ultraviolet; (320.5390) Picosecond phenomena; (320.7130) Ultrafast processes in condensed matter, including semiconductors.

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## 1. Introduction

Microchannels inside transparent bulk material play an important role for the realization of new microfluidic device concepts. Recently several new applications especially in fused silica and glass have been reported such as microfluidic optical waveguides [1], ultrafast optofluidic gain switches [2], multi-wavelength fluorescence sensors [3] and even random lasing gain mediums [4]. Microchannels are also demonstrated several times in sapphire [5–9], which has some unique properties like chemical inertness, thermal stability, high value of Young's modulus [10], a large band gap up to 8.8 eV [11] and sapphire serves as substrate for blue and ultraviolet (UV) GaN based LEDs. Having microchannels inside the sapphire substrate one might think of a monolithic liquid sensor device consisting of an LED grown on top of the wafer for illumination and a sensor on the backside of the substrate. The microchannels are such in close contact to the emitter and the detector.

Due to the large bandgap of sapphire there is no direct absorption for common laser wavelength. For material processing, electrons have to be excited from the valence band to the conduction band by nonlinear excitation mechanisms. There are two processes which play a role: Photoionization and avalanche ionization [12]. The excitation of these processes can be realized by ultrashort laser pulses in the picosecond (ps) or femtosecond (fs) range. By irradiating sapphire with pulses in the fs range, modification of the crystalline state into an amorphous phase is possible [8,13]. Based on the ultrashort laser pulse, recrystallization of the amorphous phase into a polycrystalline phase is avoided due to the fast thermal quenching. A "frozen" state of amorphous sapphire is formed, which can be etched at high etch rates by wet chemicals compared to the crystalline and the polycrystalline phase [8]. This two-step process of irradiating with fs laser pulses in the infrared wavelength range and subsequent wet etching is successfully demonstrated [5–9]. Due to the rapid progress in the development of ultrashort pulse laser, UV picosecond laser is ready for 24/7 operation in industrial environment. Hence it would be desirable to develop a process to produce microchannels in sapphire with picosecond laser pulses which to our knowledge is not yet demonstrated in literature.

## 2. Experimental setup

The irradiation process is carried out by a self-build laser-µ-machining system. A schematic diagram of the whole setup is shown in the left part of Fig. 1. A picosecond laser (Lumera Super Rapid) is used as irradiation source with three different wavelengths available (355 nm, 532 nm, 1064 nm), a pulse duration of ≈10 ps, variable repetition rate between 80 kHz and 1000 kHz, a beam quality factor of $M^2 < 1.1$ and the option for pulse on demand. The maximum average output power at 355 nm is 4.8 W depending on the repetition rate. The output power can be continuously varied between zero and maximum power by adjusting a half-wave plate combined with a polarizing beam splitter inside the laser system. The linearly polarized output beam is expanded and collimated by a Galilean Telescope to a $1/e^2$ diameter of 3.2 mm. To focus the beam, a single aspheric lens with a focal length of 10 mm is used, which is mounted on a linear translation stage to control the height of the focus (Z-axis). The sapphire substrate is placed on a vacuum chuck mounted on a high precision air bearing wafer stage. The stage exhibits a very high reproducibility of 0.1 µm in X-direction and 0.2 µm in Y-direction and has a maximum speed of 100 mm/s.

In addition, the axis system has the option to deliver output signals at fixed user defined distances, when writing any contour. This option is called position synchronized output (PSO) and is used to trigger an electro optical modulator (EOM) in the laser which selects single pulses out of the pulse train. Hence it is possible to write a contour with user-defined equidistant pulses independent of the velocity of the stage. For all of our experiments the repetition rate of the laser was set to a fixed value of 100 kHz and the speed of the axis to 4 mm/s. The PSO of the axis system is then selecting one single laser pulse out of this 100 kHz pulse train every fixed user defined distance. Hence it is possible to freely adjust the distance between the individual laser pulses (inter-pulse distance, IPD). The effective repetition rate is therefore depending on the IPD.

The system comprises also an inspection system consisting of two different microscope objectives combined with a CCD camera and a high precision optical distance sensor to measure the height of the sapphire wafer for the precise positioning of the focus below the sapphire surface. All of the components are mounted on a three dimensional granite gantry and are surrounded by a laser safety housing (not shown in Fig. 1). The irradiation process is carried out in ambient air.

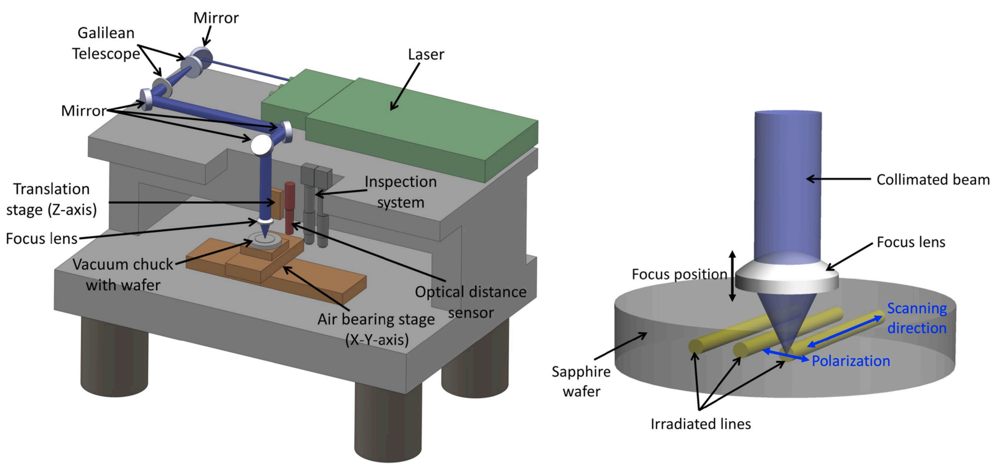


Fig. 1. Schematic diagram of the experimental setup without the laser safety housing (left) and schematic diagram of the irradiation process (right).

Two inch double side polished wafers from Roditi with a thickness of 330 µm were used as samples for irradiation. These wafers also serve as substrate material for the growth of GaN-based LEDs. Adhesive foil is attached to the backside of the wafer to absorb the radiation which is transmitted through the sapphire wafer to prevent wafer chuck ablation. The wafer is irradiated in straight and parallel 10 mm long lines, with a focus position 30 µm below the surface. The scanning direction is set perpendicular to the polarization of the laser beam, as can be seen in the right part of Fig. 1. After the irradiation process, the wafer is cleaved perpendicular to the irradiated lines to provide an easy access for the etching to the channels. The etch process was carried out in an ultrasonic bath of HF solution with a concentration of 40% at room temperature. To observe the etched channels, dark field optical microscopy with reflected light illumination (Zeiss Axio Imager.A1m) was used since the etched channels appeared wider than the irradiated non-etched lines. In order to confirm the

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formation of open channels, they were filled with fluorescence marker (BASF Lumogen F Yellow 083), dissolved in acetone, and excited with UV light. The fluorescence of the marker could be observed in the microscope. Both methods were used to determine the length of the channels.

## 3. Results and discussion

In order to achieve an etchable phase of sapphire not only the pulse duration is an important factor (fixed to 10 ps in our setup), but also the pulse energy and the IPD which both can be freely adjusted. Therefore we performed a preliminary experiment where 20 lines were written and analyzed by optical microscopy (Fig. 2). From top to bottom the pulse energy was gradually reduced while keeping the IPD on a fixed value of 2.8 µm which results in an effective repetition rate of 1.4 kHz.

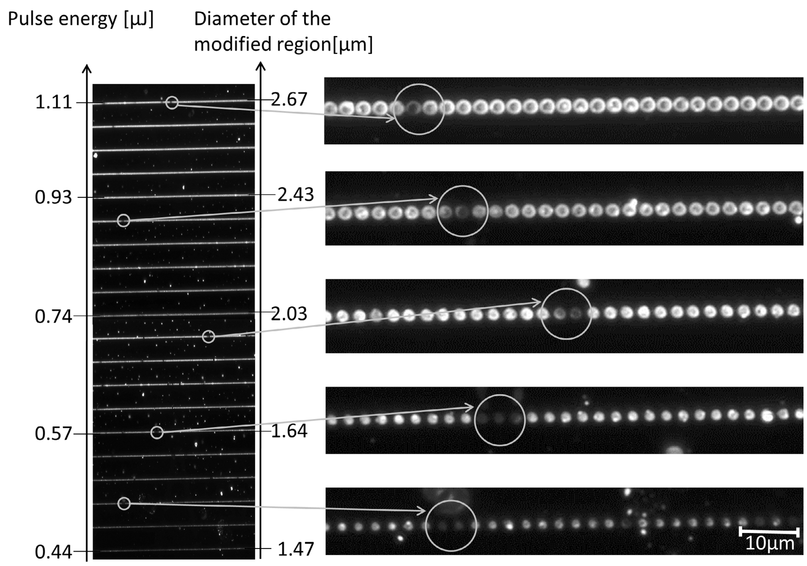


Fig. 2. Microscope image of modified regions inside sapphire realized by single laser pulses focused 30 µm below the surface. The pulse energy is gradually reduced from top to bottom while keeping the inter-pulse distance (IPD) at 2.8 µm.

Due to the large IPD, volumes modified by single laser pulses are discernible. Figure 2 shows that the volume of the modified region is decreasing with decreasing pulse energy due to the Gaussian beam profile of the laser and the constant threshold energy for modification of sapphire. Since the volume of the modified region is depending on the pulse energy, there is also an effect on the effective overlap for a constant IPD. Hence it is important to find the correct IPD for a given pulse energy to get a continuous etchable phase of sapphire. A striking point is that some modified volumes in Fig. 2 appear darker than the rest (white circles). Comparing the volumes realized by higher and lower pulse energy, it can be seen, that the brightness of the modified region is almost the same. Therefore, the reason for the darker volumes should not be caused by fluctuations in the pulse energy, which is consistent with the measured variation of less than 0.5%. Additionally the diameter of the darker modified volumes is the same than that of the brighter ones, which is a further indication that the pulse energy is the same. Due to the fact that these volumes appear darker in the dark field microscopy, the scattering of light from the microscope must be reduced, which is an indication that these volumes are less modified and potentially contain no amorphous phase.

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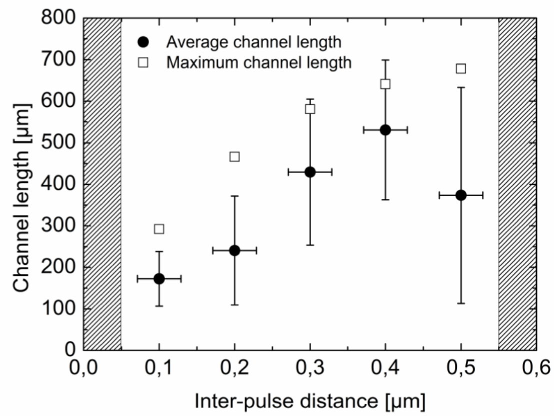


Fig. 3. Channel length depending on IPD. The shaded area on the left indicates the onset of surface ablation, whereas the shaded area on the right indicates a IPD too large to achieve an etchable line.

Figure 3 shows a plot of the channel length when varying the IPD between 0.1 µm and 0.5 µm, resulting in an effective repetition rate between 40 kHz and 8 kHz. Hence thermal accumulation effects should be avoided [6]. The pulse energy was set to a fixed value of 0.43 µJ. For the average channel length each measuring point comprises a data set of 20 lines which were etched in an ultrasonic bath of HF for four hours. The channel length was limited due to the etch time. It can be seen that with increasing IPD the average channel length is also increasing, reaching a maximum length of 530 µm at a IPD of 0.4 µm and decreasing with larger IPD. The reduced channel length at smaller IPDs can be attributed to recrystallization of the amorphous phase into the thermodynamically more stable polycrystalline phase by multipulse exposure [8]. Selecting a IPD smaller than 0.1 µm causes ablation on the surface (left shaded area), which is attributed to accumulation effects leading to ablation even at fluence levels below ablation threshold for single pulse irradiation [14,15]. Choosing an IPD of more than 0.5 µm results in non-etchable lines (right shaded area), which we ascribed to missing interconnections of the amorphous phase. Considering the standard deviation of the channel length it can be seen that the variation in channel length is increasing with increasing IPD. For a IPD between 0.1 µm and 0.4 µm the relative error remains almost the same, while a strong increase at a IPD of 0.5 µm is observed. The larger the IPD, the easier an imperfection during irradiation causes an interruption of the amorphous phase and therefore a barrier for the etching, causing a slower etch rate and therefore a shorter channel. One reason for the observed scatter might be the already mentioned darker spots in Fig. 2 which potentially have a lower etch rate. A second reason might be due to temporal jitter of the laser pulses arising from picking single pulses out of the 100 kHz pulse train causing spatial errors (spatial jitter) in the IPD. The standard deviation of the spatial error is around 30 nm and is indicated by the error bars in Fig. 3. The error caused by the axis system during the writing process (wow and flutter) is comparatively small and can be neglected. Considering the maximum channel length, it can be seen that the length is not decreasing when increasing the IPD from 0.4 µm to 0.5 µm. This can be attributed to channels containing no interruption of the amorphous phase due to spatial jitter or darker spots and therefore no stop of the etch process.

Figure 4 shows the achieved channel length when varying the pulse energy at fixed IPD of 0.4 µm. The effective repetition rate is therefore 25 kHz. Although the average channel length is nearly the same within the standard deviation it can be seen that the variation of channel length is decreasing with increasing pulse energy. This behavior has two reasons. First the modified volume is increasing due to the higher pulse energy as shown in Fig. 2 and therefore

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the overlap of the modified region is larger, equivalent to a smaller IPD. Hence it is less likely that errors in the IPD or the darker spots shown in Fig. 2 cause an interruption of the amorphous phase. The variation in channel length is nevertheless not less than 22%. Higher pulse energy caused ablation on the surface indicated by the shaded area on the right. Regarding the maximum channel length, the irradiation with the lowest pulse energy created the longest channel, which is in accordance with Fig. 3. Lower pulse energy causes a smaller modified volume resulting in a smaller effective overlap, equivalent to a larger IPD.

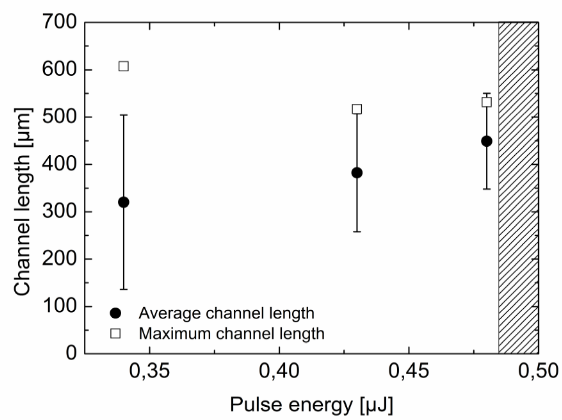


Fig. 4. Channel length depending on the pulse energy. The shaded area indicates where ablation on the surface occurs.

Due to the fact that the variation in channel length is quite high, a multi-irradiation process was investigated. Here a single line was irradiated consecutively multiple times. Therefore it is less likely that errors occurring during the varying irradiations are at the same position. Due to the high reproducibility of the air bearing stage it was ensured that again the same position was irradiated except the error due to spatial jitter along the scanning direction. The left image shown in Fig. 5 shows a dark field microscopy image of the channels irradiated with single, double and triple irradiation. For statistical analysis again a set of 20 lines were irradiated with pulse energy of 0.43 µJ, IPD of 0.4 µm (effective repetition rate: 25 kHz) and etched for 24 hours in an ultrasonic bath of HF. The narrow upper part of the lines indicate the irradiated and modified but unetched sapphire, while the broad lower part of the lines illustrate the etched channels. Each array is separated by a surface marking. It can be clearly seen that with increasing number of irradiation the variation in channel length is significantly decreasing.

The right image shown in Fig. 5 shows the results of the channel length obtained by the single, double and triple irradiation process. The standard deviation with single irradiation is 29.5% of the channel length, whereas a reduction down to 2.2% is obtained with triple irradiation. Irradiating the channel more than three times caused ablation on the surface (indicated by the shaded area). This can also be attributed to the reduction in ablation threshold by multiple irradiation caused by incubation effects [14,15]. It can be seen in Fig. 5 that the maximum channel length is slightly decreasing with increasing number of irradiations, whereas the average channel length is the same within the standard deviation. This is really astonishing since TEM investigation showed that fs multipulse exposure in the infrared forms the thermodynamically more stable polycrystalline phase [8]. Our triple irradiation process provided an average channel length of 1393 µm only limited by the etch time.

So far all the experiments were carried out having the scanning direction perpendicular to the polarization of the laser beam. By changing the scanning direction regarding the

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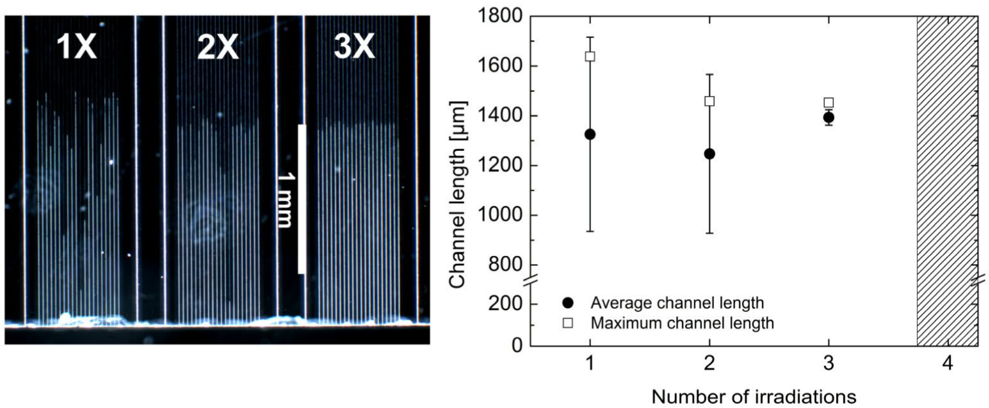


Fig. 5. Dark field microscope image of the etched channels with single, double and triple irradiation process (left). Channel length and standard deviation depending on the number of irradiations for one line (right). The shaded area indicates ablation on the surface.

polarization the achievable channel length is significantly reduced. This might be due to the formation of nanoplanes in the volume of sapphire, comparable to ripples on the surface often reported in literature [6,16,17]. Having the scanning direction parallel to the polarization, the orientation of the nanoplanes is perpendicular to the channel direction. Therefore the acid faces alternating layers of modified and unmodified sapphire, reducing the etch rate. This effect is also reported for channels produced by femtosecond irradiation in fused silica [18]. Nevertheless an etchable phase of sapphire could be produced, but the achieved channel length was more than a factor of three shorter, compared to the scanning direction perpendicular to polarization. To realize 2D and 3D structures it would be advantageous to rotate the polarization of the laser beam by means of a half-wave plate when changing the scanning direction.

By using optimized conditions with our picosecond laser system (IPD: 0.4 µm, resulting in an effective repetition rate of 25 kHz, pulse energy: 0.43 µJ, triple irradiation, scanning direction perpendicular to polarization) and an etch time of four days, a maximum channel length of 2960 µm could be achieved.

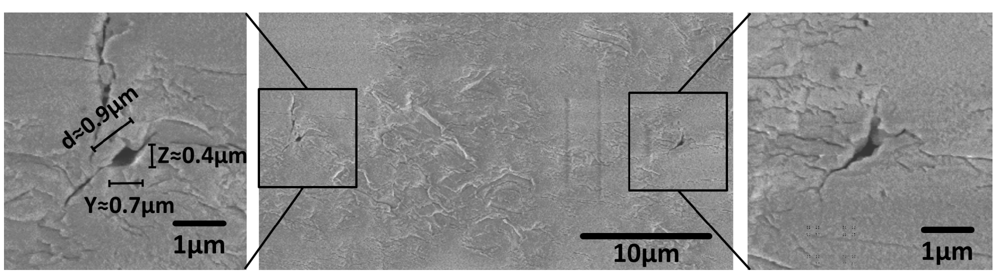


Fig. 6. SEM cross section image of a cleaved sidewall and a detailed view of two channel openings. The propagation of the laser beam was from top to bottom, while using optimized conditions for the irradiation process: IPD: 0.4 µm, pulse energy: 0.43 µJ, triple irradiation and scanning direction perpendicular to polarization and an etch time of four days.

Figure 6 shows an SEM image of the cleaved sidewall, where the cross sections of two adjacent sub-surface channels are visible, irradiated with optimized conditions and etched for four days. The propagation of the laser beam was from top to bottom. The dimensions of one channel are indicated in the SEM picture. It can be seen in the detailed view that the shape of the cross section is elongated reaching from bottom left to top right with an extension of around 0.9 µm. This results in an channel aspect ratio of more than 3200.

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Based on the optical microscope image, there is no pronounced conical behavior, even when the sample was etched for such a long time. The channel diameter is comparable with samples etched for only 16 hours. The etch rate at the beginning of the etch process is around 3.3 µm/min decreasing with longer etch time due to the diffusion limited process. To produce a liquid sensor device containing microchannels inside sapphire, it would be desirable to develop channels with larger diameters for appropriate flow rate and easier connection of an external microfluidic pump. It has been successfully demonstrated in literature that by writing several lines close to each other and therefore producing a larger modified volume with fs laser, larger channels or hollow volumes can be produced [6,7]. The next step for the future would be to demonstrate channels with larger diameter as well as 3-dimensional structures inside sapphire irradiated with UV picosecond laser and subsequent selective etching.

### 4. Summary and outlook

We have successfully demonstrated microchannels inside sapphire made by UV picosecond laser irradiation and selective etching in HF solution with a concentration of 40%. It was shown that by optimizing the inter-pulse distance (IPD) the maximum channel length can be optimized. Due to the large variation in channel length a multi-time irradiation process has been developed, which reduced the standard deviation of the channel length down to 2.2%. By using optimized conditions for the irradiation process a maximum channel length of 2960 µm could by achieved, with an aspect ratio as high as 3200. To our knowledge this is the first demonstration of microchannels in sapphire made by picosecond laser irradiation and selective wet etching. The use of a picosecond laser system, ready for 24/7 operation, the achieved channel length and the high reproducibility makes the process interesting for industrial application, for e.g. monolithic GaN-based liquid sensor devices.

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