Micro- and nanostructures inside sapphire by fs-laser irradiation and selective etching

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Abstract: The fabrication of microchannels and self-assembled nanostructures in the volume of sapphire was performed by femtosecond laser irradiation followed by chemical etching with aqueous solution of HF acid. Depending on the focusing conditions self-organized nanostructures or elliptical microchannels are produced. While the dimensions in two directions are on a micro- respectively nanoscale, feature lengths of up to 1 mm are achieved. This comes out to aspect ratios of more than 1000. This fabrication technique is potentially usable for photonic crystal based integrated optical elements or microfluidic devices for applications in life science, biology or chemistry.

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OCIS codes: (220.4241) Nanostructure fabrication ; (220.4000) Microstructure fabrication; (260.7120) Ultrafast phenomena; (320.7130) Ultrafast processes in condensed matter, including semiconductors.

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1. Introduction

The direct machining of dielectrics using short pulsed laser radiation is a promising technique for the fabrication of 3D photonic devices. By use of in-volume material modification or surface material ablation, there have been several examples for the production of passive devices like waveguides, directional couplers and splitters and even active gain components like amplifiers and waveguide lasers [1, 2, 3, 4, 5]. In addition, a combined approach of material modification followed by chemical etching provides the possibility to manufacture 3D microchannels or surface structures for integrated optical or microfluidic devices [6, 7, 8, 9]. The 3D capability for the in-volume material processing originates from the non-linear absorption of light in the transparent material. By focusing the short pulse laser beam tightly, the required intensities in excess of 10^{14}W/cm^2 for most dielectrics resulting in a highly non-linear light-matter interaction can be achieved [10]. By using pulses shorter than the electron-phonon coupling time (~picosecond order) and repetition rates <500 kHz avoiding heat accumulation, the modified area can be localized and controlled on a micrometer scale, while the surrounding material remains unaffected by the laser beam. Focusing the laser beam in the volume of a transparent material leads to a significant spreading of the intensity distribution along the beam propagation direction. The presence of an interface of mismatched refractive indices in the optical path of the laser beam causes spherical aberrations distorting the wavefront. As well as self focusing of the laser beam, this can lead to structure shapes elongated in the propagation direction [11, 12]. Etching ratios between the modified and the non-modified material of 100:1 in glass and more than 10^4:1 in sapphire have been shown [13, 14, 15]. In modified glass volumes self-assembled nanostructures (nanoplanes) perpendicular to the polarization of the writing laser beam occur and lead to a polarization dependency of the etch-rate as well as to birefringency in fs-laser written waveguides and modified areas [9,16,17]. Here we present the existence of self-organized nanoplanes in sapphire as well. Bhardwaj, *et. al.*, propose that the planes arise from local field enhancements that occur during inhomogeneous breakdown due to a memory effect arising from metastable color centers or permanent changes in electronic structure associated with chemical reorganization [18]. According to the pulse duration and the pulse energy, process windows for the production of nano-gratings and nano-grating free modifications in glass exist [19]. According to the focusing conditions, these two types of modifications are also achievable in sapphire. An influence of the pulse duration on the formation of nanostructures inside sapphire will be a topic of further investigations.

2. Experimental setup

2.1 Sample processing

Irradiation is carried out by a fiber chirped amplifier (FCPA) IMRA µJewel with a central wavelength of $\lambda = 1045$ nm, a pulse duration of $\tau_p = 400$ fs and a variable repetition rate between 100 kHz and 5 MHz. The maximum average power is $P_{av} = 1.5$ W, adjustable using a half wave plate and a linear polarizer. The beam is transferred into a microscope objective with a numerical aperture NA = 0.55 (0.8) and focused in a depth of 150 µm in the volume of the sapphire (0001) sample. The objective with NA = 0.8 allows an adjustable compensation of the spherical aberrations for a cover glass thickness between 0.1 and 1 mm. The linear spot size is approximately 1µm. To write adjacent lines, the sample is mounted on a three axes

translation stage (resolution $\Delta x = 100$ nm, maximum speed $v_{max} = 2$ mm/s) and moved along the z-axis (propagation direction of the laser is along x, Fig. 1). The used writing speed ranges from 0.1 to 1 mm/s. Since the writing speed is significantly small compared to the repetition rate of the laser, the pulse to pulse overlap is large and the laser affected zones can be considered as lines along the scanning direction. Polarization of the laser beam was set perpendicular to the scanning direction. After irradiation, the samples are lapped from both sides (parallel to the scanning direction) to remove the irregular irradiated parts due to diffraction and reflection from the samples edges. Afterwards, the sapphire is immersed in a 40% aqueous solution of HF acid for 24 hours in an ultrasonic bath. After etching, the specimen are rinsed in de-ionized water and cleaned in an ultrasonic bath of ethanol.

2.2 Sample inspection

Before etching, the size of the laser affected zone is investigated. Due to the refractive index change in the modified area, it can be observed using through light microscopy in the direction of the laser beam. After etching, the samples are investigated again by through light microscopy and SEM of the end facets to investigate the entrance of the etched microchannels. By lapping and polishing of the planes normal to the irradiated lines, cross-sections of the structures are made in a depth 100-1000 µm beneath the entrance of the microchannels and again investigated using SEM.

3. Results and discussion

In the samples irradiated with pulse energies of 0.3 to 1 µJ and repetition rates of $f = 0.5$ and 1 MHz homogeneous tracks of modified refractive index are observed by through light microscopy for a used focusing NA of 0.55 as well as 0.7 with correction of the spherical aberrations (Fig. 1, top). Sample processing with higher pulse energies leads to crack formation in the irradiated volume, for lower pulse energies no modifications could be observed. After etching for 24 hours in 40% aqueous solution of HF acid, the modified channels show a significant change in the refractive index up to a certain depth d_z (Fig. 1, bottom). SEM images of cross sections in different depths rectangular to the scanning direction confirm that the samples are etched up to d_z (Figs. 3 and 4).
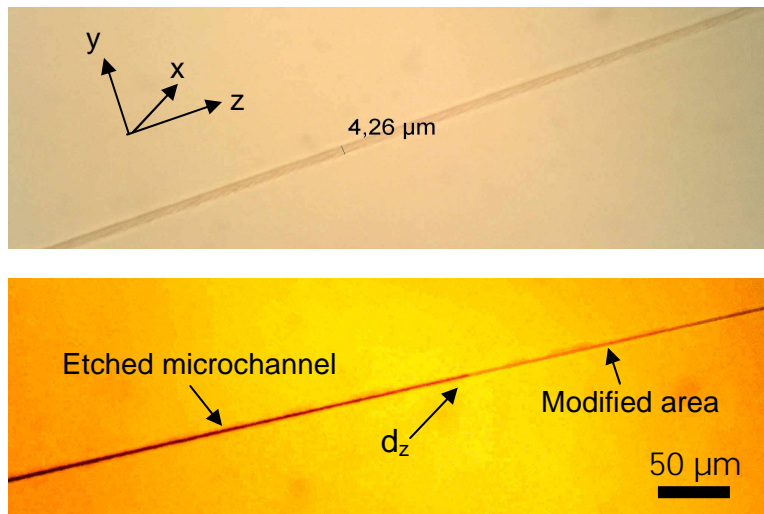

Fig. 1. through light microscopy images of the modified channel after irradiation (top) and after etching (bottom)

SEM images of cross sections deeper than d_z do not show the existence of nanostructures or microchannels. The etch depth d_z ranges between 0.5 and 1 mm, depending on the combination of pulse energy E_P, repetition rate f and scan speed v. The etch depth d_z is increasing with an increasing line energy E_Z ($E_Z = E_P * f / v$) (Fig. 2). The etch rate dependency on the line energy is qualitatively the same for both focusing conditions.
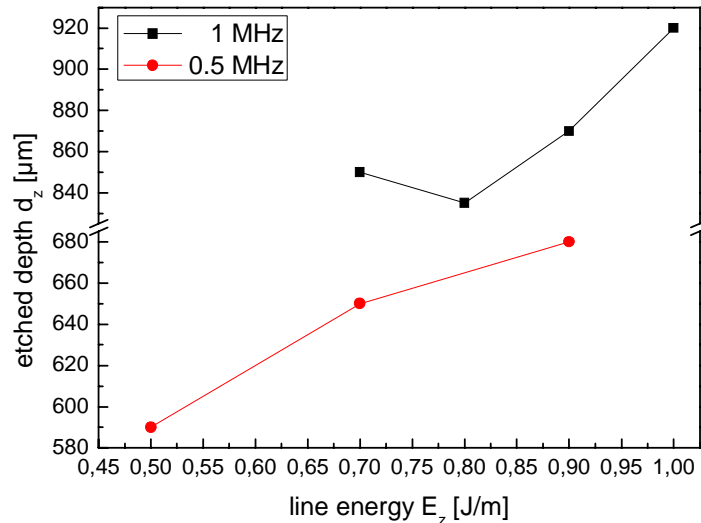

Fig. 2. etch depth d_z versus line energy for irradiation with f = 0.5 and 1 MHz (NA =0.55)

SEM images of the surface rectangular to the scan direction directly after etching make the different corrosibility between the modified part and the crystalline sapphire visible (Fig. 3, left). In the unmodified part, the surface becomes rough, but the etch rate is very small (micrometer range). The samples irradiated using a focusing objective with NA = 0.55 without correction of the spherical aberrations show the presence of self-organized nanostructures in the modified region. SEM images of cross sections in different depths up to d_z show structures of the same size and shape for all depths (Fig. 3, right). The average width of the nanostructures is about 200 nm, their distance is about 300 nm. The length is about 40 μm, compared to the calculated rayleigh length z_r = 8μm of the laser beam, the modified and therefore etched region is elongated by a factor of more than 5 by spherical aberrations and/or propagation effects (Fig. 3). The depth is at least 500 μm without interruption and permeable for liquids (e.g. the aqueous solution of HF acid and the solvent), made evident by the change in the refractive index before and after etching. We consider here the forming of nanoplanes as these structures are called by Hnatovsky and Yang, although our structures are not so well organized [9, 17]. Nevertheless, in the here presented work, the hollow nanoplanes with widths of about 200 nm are etched in one step to a depth of at least 500 μm corresponding to an aspect ratio of more than 5000.

The fabrication of hollow nanoplanes by femtosecond laser modification and subsequent chemical etching is possible using a numerical aperture of NA = 0.55 and pulse energies from E_P = 0.3 to 1 μJ at repetition rates of f = 0.5 and 1 MHz, verified by through light microscopy and the investigation of polished cross sections. In Fig. 4(c) the residue from the polishing suspension (~30-50 nm sized spheres) is visible in the nanostructures, providing evidence, that the nanoplanes have been hollow during the polishing. Using higher pulse energies leads to an increase of the size of the modified area and an increasing number of hollow nanoplanes within it, while the width and the distance of the hollow nanoplanes stays nearly the same [Fig. (4)]. A topic of further investigations will be, if a more organized and periodical formation of nanoplanes is achievable by using shorter pulse durations, as it was shown for glass [9, 17]. If these results can be transferred to sapphire, the fabrication of photonic crystal

devices with feature lengths of several millimetres for integrated optical devices seems to be feasible. The actual refractive index step between the ground material and the machined area for etched nanostructures like hollow nanoplanes is considerably higher than for the just modified material resulting in a photonic band gap, allowing smaller radii of curvature for waveguiding elements and therefore more compact devices.
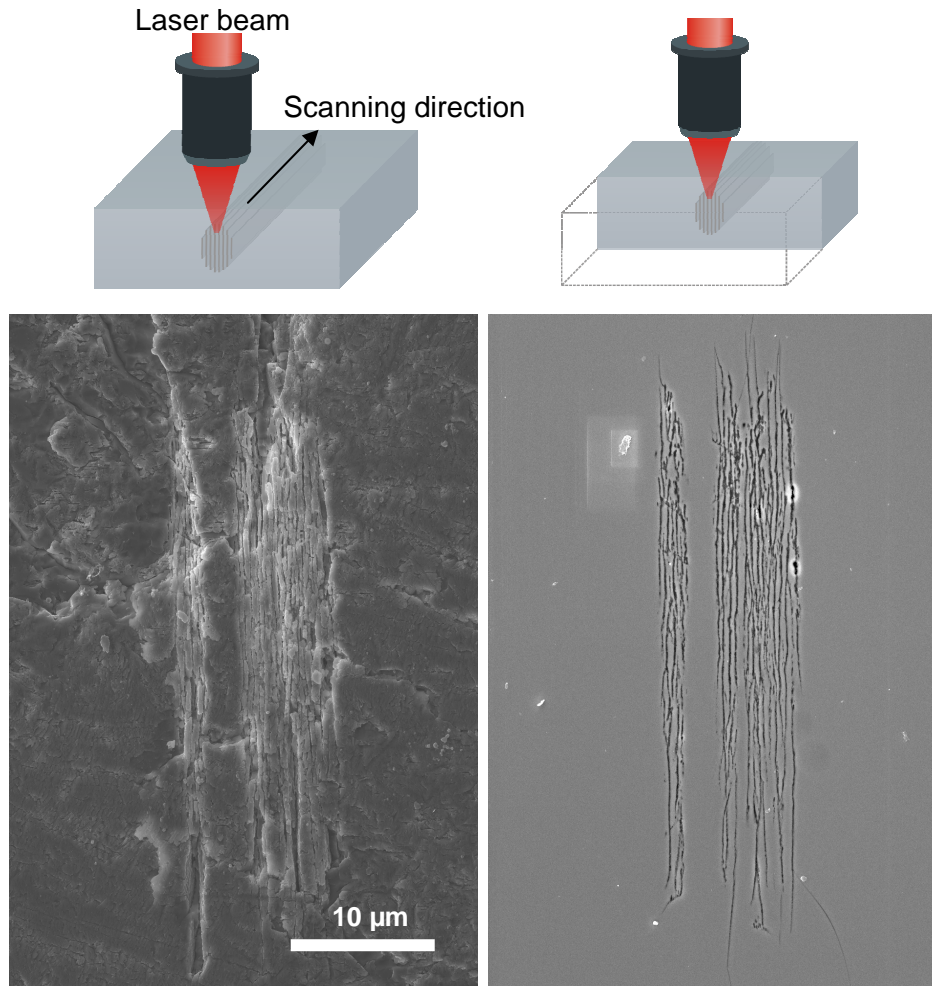

Fig. 3. SEM images of the entrance of the modified and etched channel directly after etching (left) and cross section of hollow nanoplanes in 500µm depth of the same track. Laser beam propagated from top to bottom, three parallel scans with an offset of 3 µm, focused with NA = 0.55, f = 500kHz, P = 450mW

Using a numerical aperture of NA = 0.8 and a pre-correction of the spherical aberrations for focusing can prevent the formation of nanostructures and the fabrication of elliptical microchannels with micrometer dimensions is possible (Fig. 5). The feature lengths, determined by through light microscopy are also ranging between 0.5 and 1 mm and show the same dependency on the line energy as the nanoplanes (Fig. 1). With increasing pulse energy the size of the microchannels increases from about 1 x 10µm^2 to 2 x 15µm^2 for pulse energies of E_P = 0.5 respectively 1 µJ. The part surrounding the etched microchannel in the right cross section has broken out mechanically during the lapping and polishing process. This indicates a modified region surrounding the etched channel that is not etched to this depth but less stable than the unmodified material, probably due to the presence of hollow nanoplanes.
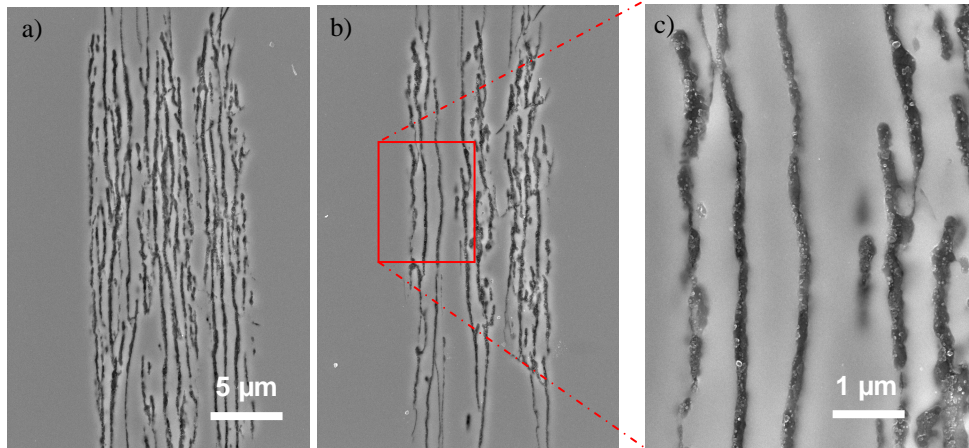
Fig. 4. SEM images of cross sections in 500µm depth, three parallel lines with NA = 0.55, f =500kHz, P = 300mW (a), P = 180mW (b+c)
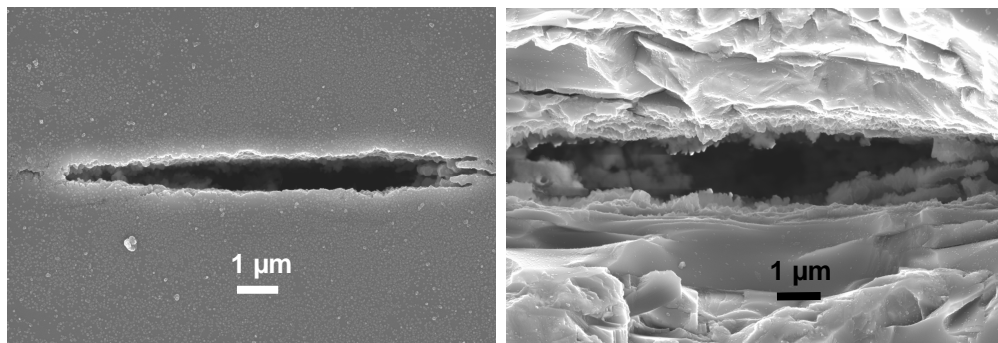

Fig. 5. SEM images of cross sections 500µm beneath the entrance of the etched microchannels, f = 500kHz, NA = 0.8, E_P = 0.5µJ (left), 1µJ (right), laser beam propagation from right to left

4. Summary and outlook

We have manufactured deep micro-and nanostructures with sub-micrometer resolution in the volume of sapphire by femtosecond laser modification followed by chemical etching with aqueous solution of HF acid. Depending on the focusing conditions the production of self organized nanostructures (hollow nanoplanes) or microchannels with elliptical shape is possible. In any case a feature length of up to 1 mm compared to dimensions in the micrometer range rectangular to the scan direction, resulting in extremely high aspect ratios is achieved. Further investigations will concentrate on the control of the shape of the nano- and microstructures. The effect of the pulse duration on the grade of organization of the hollow nanoplanes will be tested and their potential for the fabrication of photonic crystal based optical devices will be investigated. The fabrication of less elliptical shaped microchannels for microfluidic devices will be tried by a better control of the focusing conditions.