Stereolithography and 3D Micro-Structuring of Transparent Materials by Femtosecond Laser Irradiation

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ABSTRACT

We review applications of photopolymerization and photodamage by tightly focused picosecond and femtosecond pulses for the formation of three-dimensional structures. Laser microfabrication of various structures, like surface gratings, 3D optical memory, 2D and 3D photonic crystals, 3D micro-fluidic systems, etc. are described.

Microfabrication by laser irradiation provides new opportunities to realize microstructures and microdevices, highly demanded in a number of fields, e.g., microchemistry, information storage, and photonics. The background of this technique is very simple, and relies on modification of materials by intense, strongly focused laser irradiation. In this highly spatially localized region, the material may become destroyed, solidified from liquid, or otherwise photo-modified, and complex structures can be formed from many photomodified regions. Below, we describe techniques, applications, and achievements of laser microstructuring in liquid resins and solid silica glasses.

Keywords: direct laser writing, photopolymerization, silica, time-resolved measurements, light-induced damage threshold, defects

1. PHOTO-POLYMERIZATION

Photo-polymerization is used in a number of applications ranging from standard stereo-lithography (SL), 1 holographic storage, 2 to photonic crystals. 3-6 There has been an increasing demand for simple prototyping 7 which would allow fabrication of sub-μm structures. Photo-polymerization is widely used in micro-sterololithography (μSL) 8,9 for the fabrication of structures having features even smaller that the optical diffraction limit. This can be achieved through the use of optical field enhancement in the vicinity of a conducting tip 10 (a planar 2D fabrication), or by spatial scanning of a focal point of light inside the resin. In the latter case, photo-induced polymerization takes place via linear (single photon) 11 or multi (two)-photon absorption, thus allowing high resolution three-dimensional (3D) fabrication inside the resin. In the case of single-photon absorption, 3D fabrication inside the resin is possible if the non-linearity of the photo-polymerization reaction is caused by thermal conditions at the focus. 12

1.1. Photo-polymerization by Direct Laser Writing

Typical geometry of photo-polymerization experiments by a direct laser writing is shown in Fig. 1(a). We have used commercial resins, which were photo-sensitive in UV spectral region (Fig. 1(b)). The structures shown in Fig. 1(c-d) were solidified in Norocure800 (from San Nopco), the resin which showed the largest optical contrast during in situ observation of solidification process during the laser beam scanning. Laser beam with the wavelength of 355 nm was scanned in liquid resin according to the pre-programmed pattern. The pulse duration was 20 ps, the repetition rate was 10 Hz. Typical scanning speed of the stage was 4 μm/s. The threshold fluence for inducing changes observable in optical transmission of the resin was 0.9 J/cm² per pulse. This was considered as the threshold of photo-polymerization. In fabrication, typical laser fluence used was 1.4 J/cm² at the focus. A more detailed description of setup and fabrication procedures can be found in Ref. 11.
As can be seen from absorption spectrum of the resin (Fig. 1(b)), single-photon absorption was in part responsible for the initiation of the polymerization. One may expect that 3D direct laser writing in resin by photopolymerization is not feasible with single-photon absorption. However, we have found that in fact the forming resolution is even better than 1 μm, inferred from Fig. 1(d). This can be explained by the conditions of the free-radical polymerization, which requires particular thermal ambient for the successful propagation of polymerization. Evidently, those conditions are best satisfied at the focus, where photo-polymerization occurs. As a result, 3D polymerization by direct laser writing is possible even with single-photon absorption.

1.2. Assembling of Micro-structures by Photo-polymerization

Assembling micrometer-sized objects is an attractive possibility provided by the microfabrication. For this, we have developed a combined setup (shown in Fig. 2), which allowed us to establish two independently controlled laser traps, and introduce a complementary laser beam for laser-welding of the laser-trapped polystyrene beads at desired locations. At first, we have measured the laser-trapping force by dragging a laser trapped polystyrene bead in the water. The velocity, at which the bead was released from the trap is determined by the viscous drag, and can be calculated from the Stokes law. Then, two beads were trapped by two laser traps using laser power of 100-150 mW per beam, as shown in Fig. 3(a), drawn close to each other (Fig. 3(b)), and welded together at the point of contact by a single laser pulse with 355 nm wavelength and 20 ps duration. The energy density was 2 J/cm².

Figure 1. (a) Scheme of laser microfabrication setup. (b) Absorption spectra of several acrylic resins: Nopcocure800 (1), SCR701 (2), SCR751 (3), and HS671 (4). Optical density, OD, was measured in a 1 cm cuvette filled with 1 wt% 1-methoxy-2-propanol solution of resin. (c-d) SEM images of 3D structures solidified by 355 nm wavelength laser pulses of 20 ps duration in Nopcocure800.

Figure 2. (a) Setup of laser manipulation with additional possibility of laser assembling. PBS is the polarized beam splitter, DM - dichroic mirror, OL - objective lens, GM - galvanic mirrors, and λ/2 is the λ/2-plate. (b) The calibration plot of trapping force for 3.5 μm-diameter polystyrene beads.
Figure 3. Optical images of laser manipulated polystyrene beads in water. The welding of beads was made by a single 20 ps duration and 355 nm wavelength laser pulse pointed to a contact spot between beads.

Figure 4. Optical images of silica beads in water solution of acrylic acid (AA). Polymerization of AA-gel was initiated by illumination of solution with 532 nm laser pulses. One-photon photoinitiator DHBP was used at 532 nm wavelength.

Afterwards, the newly fabricated two-bead structure was re-trapped several times to make three- and four-bead structures (Fig. 3(c-e)).

We have also developed a modification of this technique, which uses laser-manipulation to make extended, flexible gel structures. In water solution of acrylic acids, photo-polymerization results in gelified material. Very low friction forces existing between gels as well as between gels and solid surfaces, make them interesting candidates for the applications in artificial joint implants, and other bio-mechanical applications. In the experiments silica beads were laser trapped and manipulated in aqueous solution of the acrylic acid (AA, 2 mol/dm³) monomers, photoinitiator, and conjugator/crosslinker. For the initiation of polymerization by two-photon absorption, the 2,2-diethoxy-1-phenylethanone (DEPE, 0.1 mol/dm³, standard illumination wavelength $\lambda < 270$ nm) was used as photoinitiator. We have also found that single-photon photoinitiator, 4,4'-dihydroxybenzophenone (DHBP, 0.8 mol/dm³), can be used as well at the same wavelength of 532 nm. The conjugator in both cases was N,N'-Methylene-bis-acrylamide (MBA) at the concentration of 0.03 mol/dm³ for two-photon, and 0.1 mol/dm³ for single-photon initiation reaction.

The trapped beads were synchronously moved along the axis aligned through their centers, and illuminated by laser pulses at 532 nm (Fig. 4). As a result, an AA-gel formed between the silica beads. The surface of the silica beads remained chemically unmodified, and the gel-silica contact was maintained solely by physical forces. However, the contact was strong enough to withstand laser manipulation forces up to 200 pN (the strength of the joint was not known to us precisely). There was no obvious difference in the appearance and flexibility of the structures polymerized using single-photon or two-photon initiation.

Further experiments were carried in an effort to produce even more complex silica-AA-gel structures. First, the contact spot between the two joined silica beads was gelified. Then, a flexible link shown in Fig. 4 was created (Fig. 5). These preliminary results show the applicability of this technique for the fabrication of complex and flexible bio-compatible structures. Modification of the glass bead surface could help to fabricate even more mechanically robust constructions.

1.3. Photo-polymerization by Femtosecond Irradiation
The same setup as discussed in Sec. 1.1 was used for fs-photopolymerization. Use of focused ultrashort laser pulses allows to increase multi-photon absorption (MPA) efficiency at the focus. This advantage was exploited in making
3D resin structures similar to those shown in Fig. 1(c,d). In some cases, prior to microfabrication the resin was presolidified by exposing it to spatially uniform irradiation in order to increase their viscosity, and to initiate free radical generation.\textsuperscript{15} Some structures were written directly (without pre-exposure) by 3D writing in liquid resin.\textsuperscript{6,13,16} Successive photo-curing was accomplished by using 398 nm wavelength exposure. Attempts to fabricate the structures at the fundamental wavelength (795 nm) were not successful due to laser induced-damage and cavitation (bubble formation).\textsuperscript{17} For this wavelength, energy density per pulse was considerably larger than 2 J/cm\textsuperscript{2} and buildup of excessive hydrodynamic pressure at the focus destroyed the material.

Despite this result, we anticipate the possibility to use high light intensities for the photopolymerization, which has not been addressed in the literature so far. When the light intensity reaches the level of the dielectric breakdown of the material, generation of white light continuum typically occurs at the focal point. The continuum, spectrally extending into UV region, can be subsequently absorbed by the liquid resin, causing the photopolymerization. Typical fluence required for the photopolymerization, 1-2 J/cm\textsuperscript{2}, is sufficient for the dielectric breakdown of most of dielectrics with laser pulses shorter than 0.5 ps. If this mechanism of photosolidification will be proved to be effective, need for a different composition of the resins will arise. In particular, practical implementation would require addition of components capable of lowering the dielectric breakdown thresholds of the resin.

2. MICRO-STRUCTURING OF SILICA BY FEMTOSECOND IRRADIATION

Photomodification in silica glass under intense, ultrashort ($\tau_p < 1$ ps) laser pulses is commonly described as a light-induced damage, and is just opposite to the photosolidification in resins. Light-induced damage destroys the glass leaving an empty in the bulk of the sample. Scanning the position the irradiated spot under conditions where two adjacent pulses spatially overlap by more than 70-90\% of their diameter, can create solid core waveguide type structures.\textsuperscript{19,20} Laser beam, tightly focused to almost the diffraction-limited focal size, can trigger a “microexplosion”

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Optical images of laser manipulated flexible silica-gel structure. One-photon photoinitiator DHBP was used at 532 nm wavelength.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Glass transition in terms of volume dependence on the temperature. The higher cooling rate causes higher glass transition temperature, $T_g$ ($T_2 > T_1$). $T_m$ is the melting temperature.}
\end{figure}
Figure 7. (a) Setup of two-pulse damage experiment of silica at 398 nm wavelength. BS marks the polarized beam splitter, R1 and R2 are the retro-reflective mirrors, M and F are mirror and filter, respectively, and DL stands for delay line. (b,c) Time dependence of second pulse energy, \( E_2 = \text{LIDT}(1) - E_1 \), necessary to observe a damage (an optical transmission is changed). The energy of the first pulse, \( E_1 \), was fixed to 0.5 \( \times \) \( \text{LIDT}(1) \) (curve 1), 0.6 \( \times \) \( \text{LIDT}(1) \) (curve 2), and 0.7 \( \times \) \( \text{LIDT}(1) \) (curve 3). Curve 4 follows the dependency \( \propto t^{3/2} \). Log-lin (b) and log-log (c) presentation of experimental data. Irradiation spot was at 50 \( \mu \text{m} \) depth.

by a single laser pulse. As a result a void core structure (or at least rarefied volume), or a voxel (abbreviation from the volume element), is created. Thresholds for both photo-modifications are similar and depend on the pulse length and properties of the glass. Qualitatively, this fits well into the glass transition scenario, illustrated by Fig. 6, and is discussed below.

Irradiation of glass with pulses having nanojoule energies creates soft or even melted material in the irradiated region and around it. Afterwards, cooling starts from the outside regions and proceeds inwards. Slow scanning of the coordinate under multi-shot irradiation results in the thermal quenching, which is fastest in those outer regions, extending along the scanning line. As shown in Fig. 6 in these regions the glass will recover from the super-cooled liquid phase earlier than at the center. The thermally quenched regions will occupy volume, larger than that at equilibrium. As this process progresses from the outer regions towards the center, the excess melted glass is forced towards the center where it finally hardens at a density higher than equilibrium. The resulting core of densified glass can be used as a waveguide.

Alternatively, single shot irradiation can create empty void-like structures in the glass. Voids result from explosions, similar to those observed in surface ablation, namely phase2' and Coulomb22 explosions. The precise sequence of events leading to the explosion is still a matter of debate. Coulomb explosion is typical run-away process occurring at the surface of dielectrics22 under ultra-short excitation. However, Coulomb explosion inside the glass may be strongly different due to the absence of material-air boundary during the ablation. The same applies for the phase explosion, since the vaporized matter has nowhere to escape.

2.1. Two-pulse Optical Damaging of Silica

Optical damaging of silica by two pulses of different polarizations, introduced colinearly into the microscope, was used to explore the dynamics of microexplosions. The pulse was divided into two by a Mikelson-type interferometer setup shown in Fig. 7(a). The damage threshold for both polarizations was the same within uncertainty of the experiment. The energy of the first pulse was fixed to a sub-threshold value, and LIDT was reached by adjusting the time delay and energy of the second pulse. Temporal coincidence of the two pulses at zero delay was verified by an interferometric autocorrelator with the precision of 0.2 ps. The results are plotted in Fig. 7. At “zero” delay contributions of the two pulses to the damage threshold are \( E_1 + E_2 = x \cdot \text{LIDT}(1) + (1 - x) \cdot \text{LIDT}(1) \equiv \text{LIDT}(1) \), where \( x \) denotes fraction of the contribution. The slope of the subsequent fast part on the dependence \( E_2 \propto t \) was about 2-3 ps. The pulse duration at the focus was evaluated to be \( \tau_p = 450 \) fs after passing through the setup (initial laser pulse was \( \tau_p = 150 \) fs). This can be seen as the recovery time of silica after the excitation by the first pulse. Obviously, lower energy of the second pulse is necessary for the damage within 100-200 ps after the first pulse.

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Figure 8. (a) Wavelength dependence of the LIDT(1). Focal point was aimed at 50 μm depth. LIDT energy was directly measured at the entrance of the objective lens. (b) Time evolution of the free carriers density, $N_{FC}$ for rectangular 120 fs duration pulses at first (curve 2) and second (curve 1) harmonic of Ti:sapphire laser. Laser fluence was 5 J/cm² in both cases (it is LIDT(1) for 795 nm at 100 μm depth). The electron-lattice energy relaxation time was taken 4 fs in simulation and initial FC concentration was $N_{FC}(t = 0) = 0$ cm⁻³. Curves 3 and 4 show critical FC density (plasmon caused reflection) for 795 nm and 398 nm, respectively. (c) Temperature dependence of the apparent diameter of transmission change in silica at $1.5 \times LIDT(1)$ at 795 nm wavelength, and at 100 μm depth. The inset in (c) show the definitions of bright (1) and dark (2) spot diameters.

Temporal position of this secondary minimum $E_2$ depends on the energy of the first pulse, and approximately follows the $\propto \text{time}^{-3/2}$ law. This can be compared with spatio-temporal profile of the temperature distribution after the excitation by $\delta$-function thermal pulse, given by the solution of the equation $\partial T/\partial t = \chi \Delta T + \text{Const} \times \delta(r) \delta(t)$. The solution is

$$T(r, t) = \frac{\text{Const}}{(4\pi \chi t)^{3/2}} \exp \left( -\frac{r^2}{4\chi t} \right),$$

where $\chi$ is the thermal conductivity, expressed in terms of mass density, $\rho$, heat capacity at constant pressure, $C_P$, and thermal conductivity, $\kappa$, by $\chi = \kappa / \rho C_P$; $r, t$ are spatial coordinate and time, respectively. This suggests that the irradiation spot is expected to cool down in time according to the $T \sim t^{-3/2}$ law, and spread according to the $r \sim (\chi t)^{1/2}$ law. The characteristic time $d^2/\chi$ shows the timescale over which temperature changes are expected to occur at the irradiation spot of diameter $d$. For silica, $\chi = 8.408 \cdot 10^{-7}$ m²/s, and taking the diffraction-limited irradiation spot diameter $d = 1.22 \lambda/NA = 360$ nm, one can find $d^2/\chi \approx 153$ ns. Much faster changes were observed experimentally (Fig. 7(b,c)) in the recovery of $E_2$. One possible explanation of these results is nonlinear diffusion, and much smaller than expected diameter of the spot excited/heated by the first pulse. This will be discussed in the next section.

2.2. Wavelength Dependence of Optical Damaging of Silica

For the measurements of wavelength dependence of LIDT(1), an optical parametric oscillator (Spectra Physics) was utilized as a tunable source of irradiation between 400 nm and 800 nm. The irradiation power was measured directly at the entrance of objective lens. Transmission of the latter varied linearly between $T = 0.85$ and 0.58 for the wavelength variation from 400 nm to 800 nm, respectively. The spot size at the entrance of the objective lens was kept the same during all measurements. The results are shown in Fig. 8(a) which plots the pulse energy at LIDT versus the wavelength. The dependence was found to be $\text{LIDT Energy} \propto \lambda$. Interestingly, the same dependence presented as the energy density (fluence) versus the wavelength, would give unexpected $\text{LIDT Fluence} \propto \lambda^{-1}$ dependence. This should be not the case for dielectric breakdown, which is a typical mechanism of LIDT for pulses longer than 20 fs, and proceeds as multi-photon seeding of the free electrons, followed by an avalanche.
This inconsistency can be explained considering the definition of LIDT fluence and intensity. Usually the fluence is obtained by dividing the the measured pulse energy by the irradiation area, calculated as $S = \pi (0.61 \lambda / NA)^2$, i.e. $LIDT_{\text{Fluence}} = \frac{\text{Pulse energy}}{S}$. In fact, the exact area where LIDT was initiated is unknown, and can be accounted for by the wavelength-dependent factor $k_\lambda < 1$. Due to the multi-photon absorption being responsible for the avalanche seeding, instantaneous intensity must be taken into account instead of the averaged pulse intensity. A single pulse of shorter wavelength tends to induce the damage faster. This means that just a fraction of the total pulse energy was consumed to reach LIDT, and this corresponds to a certain temporal part of the pulse. This circumstance can be accounted for by introducing separate factors for the contributions of the pulse energy $k_E(\lambda) < 1$ and duration $k_t(\lambda) < 1$. In order to address the exact influence of all three factors in optical damaging, further studies are necessary. The LIDT value need to be corrected by $LIDT_{\text{Fluence}} = k_E(\lambda) \times k_S(\lambda) \times k_t(\lambda)$ for fluence and intensity LIDT, respectively, where $\tau_p$ is the pulse duration. Only if these coefficients are known, the material-dependent LIDT can be evaluated for the specific wavelength.

Validity of the above given consideration can be demonstrated by the numeric simulation of free electron generation by temporally rectangular pulse with 120 fs duration (detailed description of the simulation is given in Refs. 24,25). The breakdown is reached when a critical electron density is generated. Electron escape from the irradiated volume is neglected (no recombination and diffusion). The result is given in Fig. 8(b), and shows the tendency for a shorter wavelength pulse to cause the damage earlier in time. The first, fast increasing part of FC density is solely due to the multi-photon absorption, while the second part (increasing linearly in log-lin presentation) is due to the avalanche. Tunneling FC generation is not important at the LIDT, because the light field is still < 100 MV/cm ($LIDT$ in terms of fluence, intensity and field strength is $5\, \text{J/cm}^2$, $14\, \text{TW/cm}^2$, and $86\, \text{MV/cm}$, respectively, in silica at $100\, \text{um}$ depth at 795 nm wavelength and 350 fs pulse length at the focus$^{24}$).

To answer the nontrivial question where the damage starts, temperature dependence of the spot diameter was measured at a fixed laser fluence $1.5 \times LIDT$ and 795 nm wavelength. The results are plotted in Fig. 8(c). One can see that at low temperatures the recognizable spot size was limited by the diffraction at the wavelength of observation under condensor illumination. At more elevated temperatures the spot size was proportional to $\sqrt{T}$. Assuming linear scaling of the damage spot size with the fluence, we can predict that the damage spot would be about 310 nm in diameter at room temperature (RT). This is much smaller value than that following from the theoretical diffraction limit $1.22\lambda / NA = 1760$ nm (NA = 0.55) customarily used to calculate the fluence.

Merkle and Kitriotis$^{26}$ have demonstrated that the temperature dependence of multi-photon absorption (MPA) may be approximated as $\propto \sqrt{T}$. Furthermore, the nonlinearity of the conduction band electron generation during the multi-photon excitation implies that very small change in fluence is required to produce moderate fractional increase in the electron generation rate needed to raise the material temperature to the melting point of 1880 K. Therefore, at 800 K and higher temperature the irradiation at fluence level of $1.5 \times LIDT$ efficiently generates free carriers mainly by MPA, which eventually drive micro-explosions inside silica and the recorded damage size follows the $\sim \sqrt{T}$ dependence. In fact, thermal expansion coefficient in fused silica has totally different temperature dependence with maximum at 200°C. This shows that fs pulse absorption, rather than the thermo-mechanical properties of silica predetermines the size of the damaged region.

### 3. Voxels in Silica Glass

Application of the direct laser writing technique for the fabrication of photonic crystals and microfluidic devices depends crucially on the size and shape of the photomodified region. In this section we will examine the influence of femtosecond pulse energy on the structure of voxels (volume elements).

Laser-induced breakdown occurs when a normally transparent dielectric material is transformed into an absorbing plasma at the focus of femtosecond laser pulse. Subsequent absorption by the plasma of the laser energy causes heating which leads to the permanent damage of the host material. Excitation of free carrier plasma is usually treated as a consequence of the following processes: multi-photonionization, collisional ionization of photoexcited electrons due to the Joule heating, and transfer of the plasma energy to the lattice. Large number of studies focused on the influence of these mechanisms on the laser-induced breakdown by femtosecond pulses.$^{13,27-29,25}$ Recent results indicate that during the times down to approximately 100 fs after the excitation, the role of multi-photon ionization is to supply the seed electrons. The breakdown is still completed by avalanche ionization, starting from the electron density generated by multi-photon ionization. The electrons are excited and heated faster than they transfer their excess
energy to the ions. Therefore the electron temperature may reach from few to tens of electronvolts (1 eV = 11600 K) during the laser pulse, while the ions remain relatively cold. Subsequent electron-ion energy transfer, which takes place after the laser pulse, rapidly heats the ions in an explosive manner, generating a voxel surrounded with a more/less densified material.

The laser irradiation was focused on the SiO₂ sample by an oil-immersion objective lens (×100 magnification, numerical aperture NA=1.35) in a inverted-type microscope Olympus IX70 (see 24 for more details). The irradiation fluence was varied between 0.5 J/cm² and 50 J/cm² using a neutral density filter. The pulse repetition rate was 1 Hz. Temporal pulse spreading induced by the optical elements used in the setup was carefully estimated. According to Hanninen et al.³⁰ high NA objective and the tube lenses broaden 140 fs pulses to the duration of about 240 fs. A 2D scanning stage with 0.1 μm resolution was employed for the sample scanning along the X and Y directions. The fabrication was monitored with a CCD camera (Sony DXC-930) and a monitor (PVM-1442Q). Samples of dry v-SiO₂ of EDC-brand (Nippon Silica Glass Co.) with the hydroxyl group OH concentration less than 10 ppm were used in this experiment.³¹ The width and thickness of the silica slabs were (250 ± 20) μm and (140 ± 20) μm, respectively. Both sides of the samples was polished to enable observation of the fabricated structures through the side surface. In all experiments fs irradiation was focused at 20 μm depth. The resulting voxels were examined using a confocal laser scanning microscope (Zeiss, LSM-410) with maximum lateral resolution of about 0.25 μm (×100 magnification, numerical aperture NA = 1.35, for λ=488 and 514 nm) at a cross-section of interest.

In our work, determination of single-pulse LIDT was done by direct in situ optical observation under the microscope objective with NA = 1.35 and about 398 nm spatial resolution (i.e. the lateral resolution attainable under condenser illumination). LIDT was determined as the power level at which 75% of all laser shots leave observable changes in the optical contrast of the sample. According to this definition, LIDT values lower more than 8 times than those reported by Du et al.,²⁷ and comparable to the recent results of the Mazur group,²⁰ were determined. The lowest single-shot bulk LIDT fluence measured by this method was 1.28 J/cm² (5.2 nJ) for 240 fs pulses.

To visualize the structural changes induced by the laser pulses of different energy we made arrays of voxels and examined the arrays by confocal microscope. Figure 9 shows side and top view images of voxels produced by pulses.
Figure 10. Energy dependence of the axial length (a) of the voxel (open squares), filaments (solid squares), and diameter (b) of the voxel. Lines serve as eyeguides.

of about 1.2×LIDT (a-b) and 3.7×LIDT (c-d) energy. In both cases the pulse propagation is from top to the bottom as indicated by the arrow. The dependence of the photomodified region dimensions on the energy of the femtosecond pulse is summarized in Fig. 10. The images illustrate that voxels are cylindric in shape regardless of the irradiating pulse energy. The smallest voxels have 0.39 μm diameter and about 0.5 μm length at fluences close to the LIDT. Both sizes increase with pulse energy. It is important to mention here, that diffraction-limited beam diameter at the focus is \( d = 2w_0 = 0.733 \lambda/NA = 0.432 \mu m \) (FWHM). Therefore, the photomodified area, capable of effective light scattering, is smaller than the diffraction-limited spot size even at 2×LIDT. Furthermore, our results indicate that formation of filament and ring structure has a well defined threshold of about 6 nJ. It is also important to notice the nonlinear dependence of the length of the filament and voxel diameter on the pulse energy. Saturation is clearly observable for 2-2.5×LIDT pulses. In contrast, the axial length the voxel depends linearly on the irradiating pulse energy, and gradually approaches the confocal length \( z_{con} \). The filament diameter stays nearly constant with pulse energy, and is close to the resolution limit of the confocal microscope.

3.1. Discussion of the expected voxel dimensions

The beam spot size \( w \) after passage through the focusing optics is a function of the axial position \( z \) and the confocal parameter \( z_{con} = 2z_R \), which is characterized as follows (all at 1/e² intensity level):

\[
z_{con} = \frac{2n}{\lambda} \frac{\lambda}{NA^2} ,
\]

\[
w(z) = w_0 \left( 1 + \frac{z^2}{z_R^2} \right)^{1/2}.
\]

here \( \lambda \) is the irradiation wavelength, \( n \) is the refractive index of the material, and \( z_R \) is the Rayleigh length. For our experiments \( \lambda = 0.795 \mu m, n = 1.473, \) and \( NA = 1.35, z_{con} = 1.29 \mu m \). The pulse irradiance at the focal point \( I(r, z, t) \) then can be then expressed as

\[
I(r, z, t) = I_0 \text{sech}^2 \left[ 2 \ln(1 + \sqrt{2}) \frac{t}{\tau_p} \right] \frac{\exp \left[ \frac{-2r^2}{w_0^2 \left[ 1 + \frac{2z}{z_R} \right]^2} \right]}{1 + \left( \frac{2z}{z_R} \right)^2},
\]

where \( I_0 = \frac{P_{max}}{\pi w_0^2}, P_{max} \) is the pulse peak power, \( \tau_p \) the pulse duration (FWHM). Usually, the laser power \( P \) is a function of time, while the intensity depends on both time and the irradiated area. However, for the femtosecond
pulses, the spatial extent of the pulse \( l_p = c T_p \sim 72 \mu m \) (for a 240 fs pulse) may be comparable or even less than the focal region. Therefore, the laser power is both time and space-dependent. The parameter \( N_z \) is typically used to characterize the ratio of the pulse spatial extent to the focal region\(^{32}\):

\[
N_z = \frac{l_p}{z_{conf}}.
\]

Under our experimental conditions, \( N_z \gg 1 \), and the laser pulse is much longer than the focal region. Thus, spatial variation of the pulse shape can be ignored, but for \( N_z \ll 1 \), spatial and temporal propagation must be considered. As we can see from Eq. 4, for waist of a tightly focused laser beam is comparable to the Rayleigh length. Since the intensity decays falls exponentially \((\exp(-r^2))\) in the radial direction, and quadratically \((z^2)\) in the axial direction, the effective shape of the breakdown region reminds a thin cylinder (Fig. 11). It follows from this approximation, that the breakdown area will become longer with increasing pulse intensity, as indeed was observed experimentally (see Fig. 10(a), open squares).

The presence of filaments is an indication of self-focusing. In our experiments laser irradiation power was varied from 19 kW till 0.2 MW, whereas threshold for the filament formation was 25 kW. The critical power for self-focusing in EDC-brand silica is \( P_{cr} = \pi(0.61)^2A^2/8\pi n_0 n_2 = 1.38 \text{ MW} \), where \( n_2 = 4.543 \times 10^{-16} \text{ cm}^2/\text{W} \). This means that Kerr nonlinearity can not cause the formation of the voxel tails. This is not surprising, because the expression given above is valid only in the paraxial approximation. In the case of femtosecond irradiation, focused by a high NA objective, the transverse size of the pulse becomes comparable or smaller than the wavelength \((\lambda \leq \lambda_0)\). In this case, correct description of the nonlinear optical pulse propagation must include higher diffracted orders into the self-focusing equation, which can only be solved numerically.\(^{33}\) Another possibility of self-focusing is due to the plasma density gradient. The threshold for laser power for nonlinear force self-focusing in plasma\(^{34}\) is

\[
P = 1.15 \times 10^4 T, \text{ for } \omega_p \ll \omega,
\]

where \( P \) is laser power in W, \( T \) is plasma temperature in eV, \( \omega \) is the laser radiation frequency, and \( \omega_p \) is the plasma frequency. According to this model, the nonlinear force accelerates plasma in the radial direction of the beam, producing lower density at the center, thus causing focusing. Plasma temperature was determined from its time-integrated emission spectrum which had a peak around 2.39 eV, corresponding to the blackbody temperature of about 9000 K. However, it is quite possible that the measured emission may emanate from the surface of the plasma region due to plasma shielding, and thus would not represent its internal temperature. Substituting the measured temperature into Eq. 6, we obtain the self-focusing threshold power of about 9 kW. Quoix et al.\(^{35}\) have recently demonstrated that during the ablation of silica surface by 120 fs pulses, maximum plasma temperature is
about 20 eV, and the corresponding critical power is $P = 0.25$ MW. This indicates that beam self-modulation effects should be included into the treatment of our experimental results. Self-focusing at the focus of high NA objective is currently being investigated.

Thus, the above given data and discussion show that voxels, created in silica by tightly focused pulses have shapes of thin cylinders. Furthermore, at pulse energy above $1.2 \times \text{LIDT}$ the shape is influenced by self-focusing.

4. CONCLUSIONS

We have described principles and applications of photopolymerization for direct laser writing of 3D structures. Tight focusing of femtosecond and picosecond pulses enables to fabricate structures with feature sizes approaching the diffraction limit of the optics used. The high resolution of laser microfabrication is not compromised by the presence of significant one-photon absorption. Movable joint-like structures can be fabricated using a combination of laser microfabrication and laser trapping techniques.

Very similar technique can be also used for a 3D laser microfabrication in silica. Our two-pulse experiments demonstrate thermal contribution to the dielectric breakdown. Influence of self-focusing even in the presence of tight focusing is demonstrated.

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REFERENCES


