Femtosecond laser-assisted three-dimensional microfabrication in silica

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We demonstrate direct three-dimensional (3-D) microfabrication inside a volume of silica glass. The whole fabrication process was carried out in two steps: (i) writing of the preprogrammed 3-D pattern inside silica glass by focused femtosecond (fs) laser pulses and (ii) etching of the written structure in a 5% aqueous solution of HF acid. This technique allows fabrication of 3-D channels as small as 10 μm in diameter inside the volume with any angle of interconnection and a high aspect ratio (10-μm-diameter channels in a 100-μm-thick silica slab). © 2001 Optical Society of America

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Recently, there was great interest in the application of laser microfabrication to the fields of micro-optics, microelectronics [photonic crystals, three-dimensional (3-D) optical memory], and microchemistry. For example, microfabricated microchannel chips have been applied to microfluidic devices for liquid chromatography, flow injection analysis, and electrophoresis.[1,2] Channel chips are also expected to play important roles in microreactors and in structures for micrototal-analysis systems (μ-TAS's). Miniaturization of systems for chemical analysis can lead to improved efficiency with respect to sample size, response time, and reagent consumption.[3] In most cases, chips are fabricated on a silicon or glass substrate by use of planar technology, which is a multilayer and multistep approach consisting of photolithography, imprinting, etching, sputtering, and the like. Former attempts at 3-D microfabrication in glassy materials have required photosensitive glass,[4] the elaboration of which is complex. Moreover, the stability of channels for various chemical reagents in μ-TAS's is essential for control of the flow of these reagents under chemical reactions. Thus the contamination that typically occurs in microchannel fabrication following planar technology that uses sacrificial layers or the chemically active walls of photosensitive glass has hampered the operation of μ-TAS's.

In this Letter we demonstrate, for the first time to the best of our knowledge, the solution of this problem by direct intravolume 3-D microfabrication in high-purity silica glass. The whole process was carried out in two steps: (i) writing of a preprogrammed 3-D pattern inside silica glass by focused femtosecond (fs) laser pulses and (ii) etching of the optically damaged silica in a 5% aqueous solution of HF acid. The advantages of this approach include higher fabrication speed of the 3-D structure and optical transparency, which allows one to employ optical characterization such as photoluminescence, absorbance, or Raman scattering at any location of the μ-TAS chip, with the resolution determined by the focusing optics.

Samples of dry silica (the concentration of the hydroxyl group, OH, was less than 10 parts in 10^6) were irradiated in an optical microscope by focused fs-laser pulses through an oil-immersion objective lens with 100× magnification and a numerical aperture of 1.30. The width and thickness of the silica slab were (250 ± 20) μm and (140 ± 20) μm, respectively. The irradiation spot size inside the silica glass was evaluated to be $\sim$0.75 μm. We used a fs laser system that generates and amplifies 795-nm-wavelength pulses at a repetition rate of 1 kHz with a pulse width of approximately 120 fs (FWHM) to damage the silica optically. The irradiation intensity was varied from 14 TW/cm^2 (the measured intravolume light-induced damage threshold value) to 56 TW/cm^2 by a neutral-density filter attenuator. A mechanical scanning stage with 0.5-μm resolution in the x, y, and z directions was employed for sample scanning. The resulting 3-D pattern was examined with a laser scanning microscopy with lateral resolution of 0.47 μm (for 488-nm radiation), and 3-D structures were viewed at any cross section of interest. A more-detailed description of the procedure of fs fabrication can be found in Ref. 5.

We transferred a preprogrammed 3-D pattern to the silica volume (see Fig. 1) by producing uniformly distributed damage spots made by multiple shots when the sample was translated in x, y, and z directions. The whole fs-laser fabrication process was accomplished in $\sim$2 min. After laser microfabrication, the sample was developed in a 5% aqueous solution of HF under ambient conditions. The total

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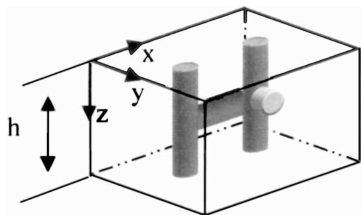

Fig. 1. Schematic configuration of 3-D pattern, which was written by focused fs-laser beam inside silica by scanning of the sample along the x, y, and z axes. The light propagated along the z axis. The pattern was created by multiple-shot irradiation with pulses of 4 times the laser-induced damage threshold intensity. h is the length of the vertical channel.

etching time was ~3 h. During etching, the sample was periodically examined under a laser scanning microscope. This allowed us to determine etching rates precisely and to observe the etching dynamics of laser-damaged and undamaged silica. Here the term etching rate refers to the difference in diameter of the etched channel for each consecutive etching hour. The top and side views of the resulting 3-D pattern after irradiation with fs-laser pulses of ~4 times the laser-induced damage threshold intensity followed by HF etching for 2 h are depicted in Figs. 2(a)–2(c). For comparison, a side view of the developed pattern after 3 h of etching is presented in Fig. 2(d). As can be seen from Fig. 2, the 3-D structure formed from the horizontal and vertical cylinder channels was successfully fabricated inside the silica glass. The horizontal channel was initially formed 40 μm from the glass surface. The initial diameter of a multiple-shot damage spot at the glass surface was nearly equal to the nearly diffraction-limited spot size of 0.89 μm. Starting from that submicrometer-sized voxel (volume element; the smallest optically damaged volume per shot), straight vertical channels with a maximum opening diameter of approximately 12 μm were formed in the sample after 3 h of etching. The length of these channels was ~120 μm. As shown in Figs. 2(c) and 2(d), the cross sections of the channels at the surfaces were larger than those inside the glass (near the middle of the silica slab) by ~5%. This difference is due to the fact that the glass surface and the channel openings were exposed to the acid solution longer than was the inside of the glass. The observed changes in the channel diameter near the surface of the sample are summarized in Fig. 3. It should be pointed out that the highest etching rate of 6.5 μm/h was observed between the first and second etching hours in the case of the diameter of the vertical channels. After the first etching hour, we clearly observed a deep (70-μm) penetration of the acid solution into the silica along the vertical channels of the fabricated pattern owing to capillary force. This particular feature allows the fabrication of high-aspect-ratio structures, if one considers that the ratio of the acid penetration depth to the change in the channel's width was ~20 times larger during the first hour of development than during the second. Thus the fast second-hour etching results from a combination of two factors during the preceding hour of development. First, the vertical channel openings started to develop, and second, extremely fast penetration of the acid solution occurred along the vertical channel. From our experimental data, it follows that the etching rate of the undamaged silica remains constant and equals approximately 4.5 μm/h for a given concentration of acid. This assumption allows us to conclude that, in our case, the optimum etching time for 3-D pattern fabrication was 2 h; during the next etching hour, we observed only increasing of the channel width at an etching speed nearly equal to that in undamaged silica. It is noteworthy that the channel interconnection angles remained unchanged during etching, a feature that is especially favorable for complex 3-D pattern fabrication. For applications in the field of chemistry in small domains (micrometer sized), there are certain requirements regarding the roughness of the microfabricated pattern.[6] The measured roughness of the sidewalls of separate vertical channels was accordingly 0.96 and 1.6 μm after 2 and 3 etching hours, respectively (Fig. 2). We attribute this variation in the sidewall roughness to

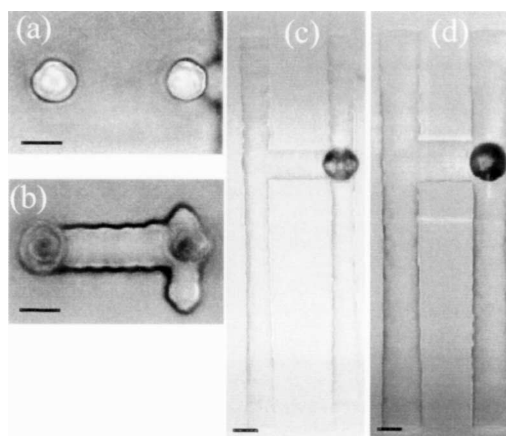

Fig. 2. Optical transmission images of the 3-D structure obtained on samples after 2 h of development in an aqueous solution of HF acid: (a) top view of the plane (xy) of the beam entrance, (b) top view of the horizontal channel at a depth of ~30 μm, (c) side view (zy plane) of the whole 3-D pattern, (d) side view of the 3-D pattern after 3 h of development. Scale bar, 7 μm.

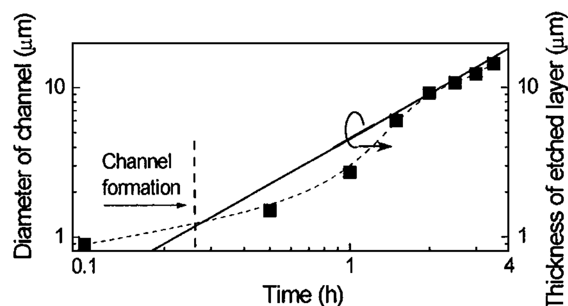

Fig. 3. Etching rate of silica. The dependence of the diameter of the vertical channel (left-hand scale) versus etching time and the uniform etching rate of the silica surface (right-hand scale). The dotted curve is a guide for the eye.

the nonuniform dose of irradiation accumulated as the sample was moved along the z axis during the multiple-shot laser microfabrication. Application of a buffered HF solution should result in even smoother internal surfaces where the access of fresh acid to those surfaces is hampered.

To clarify the observed mechanism of the etching phenomenon let us consider a simple qualitative model. As mentioned in Refs. 5 and 7, when the deposited laser radiation power exceeds the optical damage threshold, microexplosion of the silica sample takes place at the focal point, where multiphoton absorption first generates free carrier plasma, which further absorbs light and results in secondary ionization of the silica. The whole process was accompanied by strong supercontinuum generation, which soundly indicates that strong coupling between laser radiation and highly excited silica was taking place. Typically, as a consequence of microexplosion the focal region is surrounded by a shell of densified material. Such a structure exhibits the signature of a high-pressure wave that forces melted material from the center of the explosion outward.[8] In the current literature there are several descriptions of ultrashort laser-pulse interaction with transparent dielectrics[9] and laser-induced pressure-wave (i.e., shock-wave) propagation in silica glass.[10,11] These previous reports indicate that pressure waves may be a causative factor of densification, and even of limited destruction of the silica. Postshock examination of the samples indicated that modifications in the structure arose from changes in the average (144°) $O_3 \equiv Si-(O)-Si \equiv O_3$ bridging angles of the SiO_4 tetrahedrons.[12] The decrease of the bridging angle in densified silica increases the reactivity of oxygen because of the deformed configuration of the oxygen's valence electrons. Such configuration deformation could be considered in terms of the Lewis base, which is more chemically active in reactions with acids than in materials such as undensified silica. Under our experimental conditions, we can expect an approximately 10% increase in the silica density around the microexplosion site. Thus it can be expected that the etching rate of the fs-laser-irradiated pattern in the silica will be higher with respect to the etching rate of undamaged silica. This expectation applies even in the more-dense silica surrounding the microexplosion site, because the densification is related to the decrease in the average bridging angle, which leads to greater exposure of the silica to the acid. Further investigation on this matter is underway.

In conclusion, we have demonstrated the possibility of 3-D microchannel fabrication inside silica achieved by a simple two-step procedure involving fs-laser irradiation and subsequent etching. The etching solution can be optimized for rapidity or smoothness of etching. By extension, the method can be applied for large-scale (millimeter-to-centimeter) fabrication, in which the optical damage is introduced along the edges of the 3-D structure (perforationlike marks are recorded along the edges of the volume to be removed) and is later removed by etching.

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