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Microstructuring of Silica and Polymethylmethacrylate Glasses by Femtosecond Irradiation for MEMS Applications

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ABSTRACT

We report the fabrication of complex 3D microstructures in silica and polymethyl-methacrylate glass by a combination of femtosecond laser microfabrication and chemical wet etching techniques. It is demonstrated that fabrication of interconnected network of channels having lengths of about 200 μm, and diameters as small as 10 μm is possible due to the enhanced etching selectivity (typically 20 - 60) in the laser-irradiated regions. Thus, it becomes feasible to form 3D micro-fluidic and photonic crystal structures in transparent glass-like materials using this approach. In addition, preliminary results on microstructuring of rubber are presented.

INTRODUCTION

Ever increasing need for miniaturization of various mechanical, optical and electrical devices creates demand to increase the spatial resolution of currently available microfabrication techniques. As far as pulsed lasers are involved in the microfabrication, this demand is transformed into the requirement for lower wavelength and shorter duration pulses. For a fixed laser wavelength, lateral resolution of the microfabrication can not be increased infinitely without compromising the axial resolution [1]. Thus, shorter laser wavelengths, possibly expanding to XUV and X-ray regions will be needed in order to scale down the minimum feature size. In the most foreseeable future eximer lasers are a likely choice , e.g., KrF laser (λ = 248 nm) is already used commercially for lithography with 130 nm resolution, also ArF and and F_2 lasers emitting at 193 nm and 157 nm are available. It is necessary to stress here, that similar, albeit slightly longer wavelengths are also achievable with widely popular femtosecond solid state laser systems (e.g., Ti:Saphire) by higher harmonics generation [2]. In fact, use of such systems has proven indispensable in pushing the spatial resolution of the microfabrication beyond the diffractive limit [3,4]. In this work we demonstrate the capabilities of femtosecond laser microfabrication, which may be further enhanced by combining it with wet chemical etching. Although such approach does not guarantee very high spatial resolution, it enables one to obtain high aspect ratio channel-like microstructures, highly demanded in photonic and microfluidic applications. We report the fabrication of such prototype microstructues in silica and polymethylmethacrylate (PMMA) glasses.

EXPERIMENTAL DETAILS

The microstructuring experiments were carried out using τ_p = 150 fs, λ = 800 nm (or 400 nm) pulses of a Ti:Sapphire laser. Laser irradiation was focused inside the samples by a high numerical aperture microscope objective lenses with NA = 0.8-1.35 to the depth of 5-150 μm

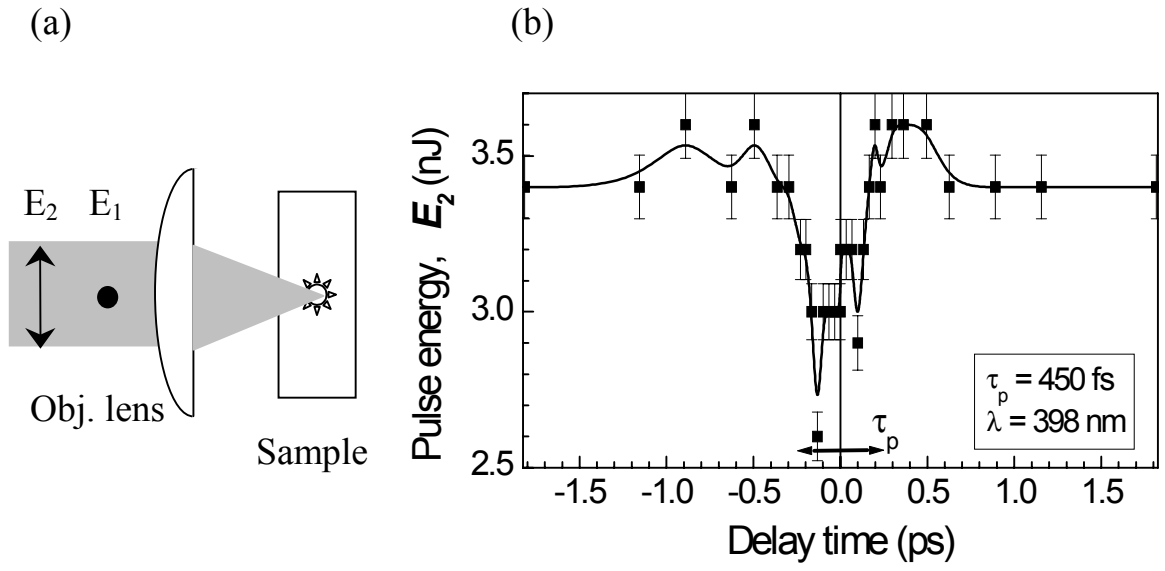

Figure 1. (a) Sketch of the experiment with two mutually delayed pulses, note the different linear polarization of the two pulses, (b) dependence of the second pulse energy, required to reach the LIDT on the delay time. The energy of the first pulse is constant ($E_1 = 0.5 \times LIDT$ = 2.6 nJ).

from the surface. The pulse intensity was within 2-200 nJ range, and was adjusted to exceed the light-induced damage threshold (LIDT) value. The pulse duration at the focus was evaluated to be 350 fs, taking into account temporal stretching in the focussing optics and the sample. The optical damage was monitored by *in situ* observation through the same microscope lens under white light illumination. The damaged spot size was typically within the $\lambda/2$ to λ range, depending on the focusing depth and pulse intensity. The extended microstructures were drawn from many overlapping damage spots, recorded in a computer-controlled sequence at precisely controlled locations. The spatial overlap between adjacent spots was significantly larger than the radius of a single damaged spot. After the laser microfabrication, the recorded channels were developed by wet etching. For silica we have used 5.4 wt% HF aqueous solution, stabilized at 25° C. Etching of PMMA was carried out in water solution of methyl-iso-butyl-ketone (MIBK) 1:20 by volume under ultrasonic shake for 5 min. The developed patterns were examined with a confocal laser scanning microscope (LSM) with maximum lateral resolution of 0.25 μm (NA = 1.35, at λ = 488 nm). For better visualization, in some cases the channels were filled by a 10 mM Rhodamine water solution. This was done by placing the sample in an aspirator at low vacuum for 15 min. Subsequently, channel luminescence image under 540 nm excitation was examined with the LSM.

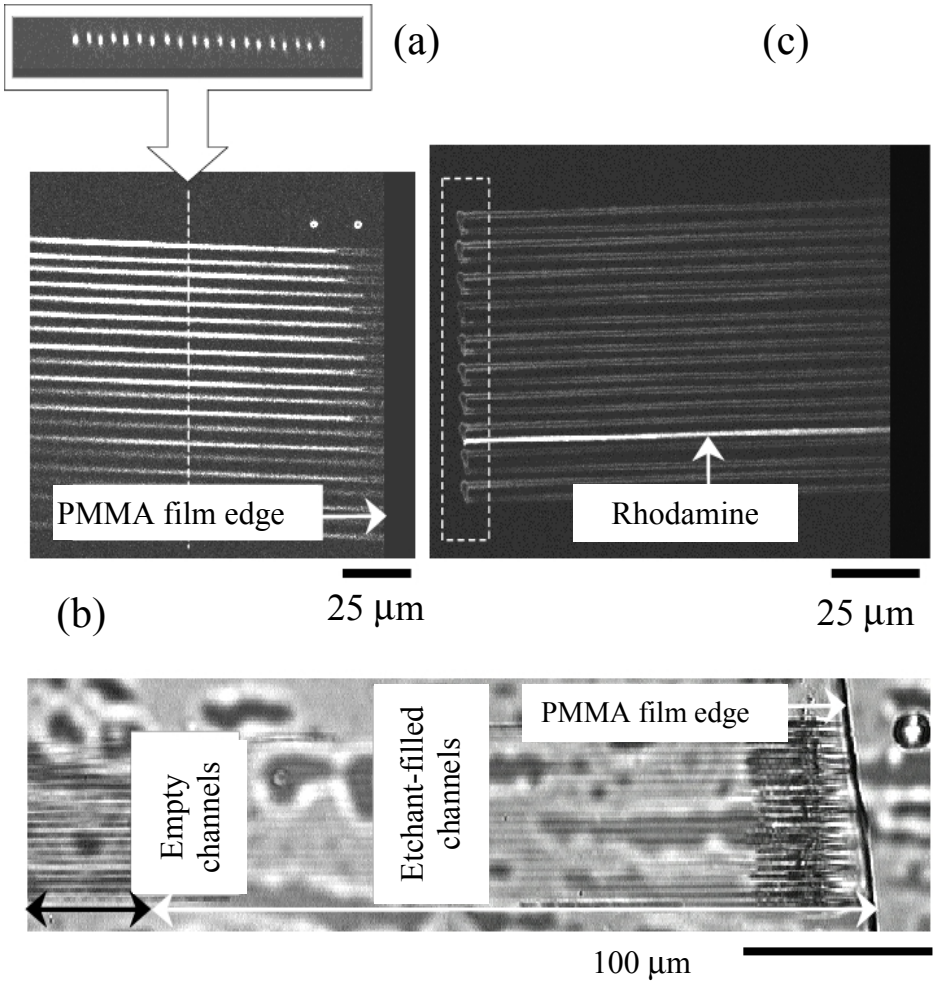

Figure 2. (a) Confocal optical image of the laser fabricated channels in PMMA film after wet etching in a MIBK solution. The inset on the top shows the side cross-section image of the channels. (b) Optical image of the channels partly filled with etching solution. (c) Confocal optical image of rhodamine filled channel wet etched in PMMA. Confocal images were obtained in 488 nm wavelength illumination.

RESULTS AND DISCUSSION

Microfabrication in PMMA

To better understand the dynamics of laser microstructuring in PMMA, we fabricated it using two spatially overlapping pulses with a controllable time delay between them (Fig. 1(a)). The two linearly cross-polarized pulses were incident on the sample collinearly in a Mikelson-type interferometer with a delay line in one arm. Pulse duration in the focus was about 450 fs. Figure 1 (b) shows the dependence of the second pulse energy, required for the damage to occur, on the pulse delay time. The dependence is quite expectedly symmetrical with respect to zero

delay. The two dips are most probably caused by cross phase modulation of the two pulses at the focus. This result infers excited state recovery time shorter than 1 ps after the excitation by ½ LIDT intensity pulse. This value of the recovery time in PMMA is very close to that measured in silica [5]. The pulse energy required for the damage was found to be polarization-dependent. For one beam polarization (labeled as E_1 in Fig. 1) LIDT is (5.2±0.1) nJ, while for the other one LIDT is (6.3±0.1) nJ. This result can be understood in terms of the electric field summation at the focus [6].

Figure 2 shows the channels recorded in PMMA at 2.2 LIDT intensity, and subsequently wet etched. The wider openings of the channels are apparently the result of laser ablation, revealed even better by the etching (Fig. 2(a)). The Image of the Rhodamine luminescence (Fig. 2(c)) indicates just a few channels filled with the Rhodamine solution. Closer inspection has revealed that most of the channels were blocked (especially at the turning points indicated by a dashed box in Fig. 2(c)). The most likely reason for the blockage is the polymer swelling at the channel walls, which occurs after the wet etching, because the etching solution acted as a solvent for weaker cross-linked polymer networks. Photoluminescence images indicate channels as thin as 2 μm in diameter.

Micro-channels in silica

As we have reported previously, wet etching of optically damaged silica can be used for microfabrication of interconnected channel structures [7].Difference between the etching rates of optically damaged and unaffected regions makes possible fabrication od 3D structures. Earlier findings indicate different etching contrast for different HF-based etching solutions [8]. The laser damaged densified/rariefied shell surrounding the focal spot, is etched at a significantly different

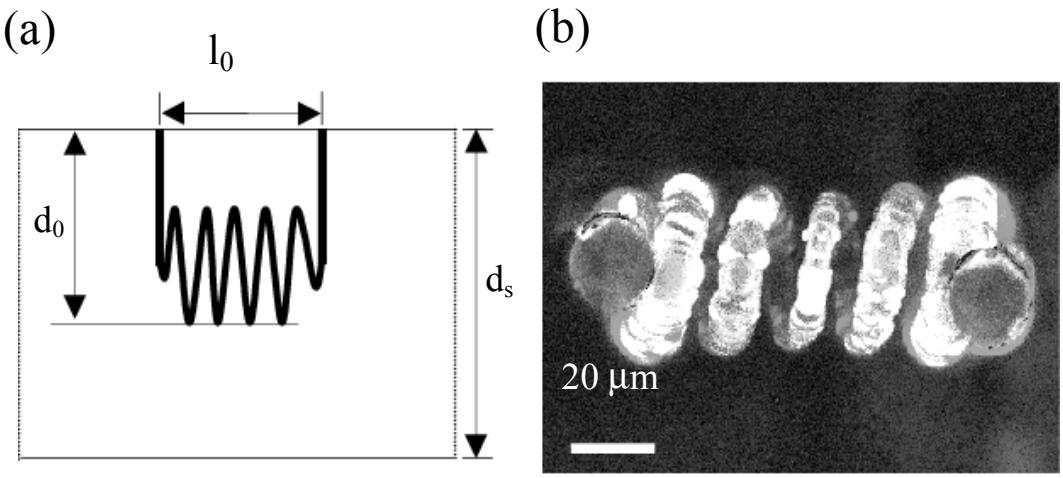

Figure 3. (a) Sketch of a 3D spiral pattern, written in d_s = 250 μm thick Heraus glass by focused fs-laser beam by scanning the sample in 0.6 μm steps along x, y, and z directions. The fabrication depth d_0 was about 50 μm, radius of the spiral 14 μm, and the pattern length l_0 = 80 μm. The fabrication was performed with 3 LIDT pulses. Subsequently the structure was etched in a 5% HF solution for about 7 hours. (b) 3D luminescence mapping image from Rhodamine solution permeated inside the channel.

rate than the unaffected material. Furthermore, micro-cracks left after the ultrafast photomodification of explosive character enhance the delivery of etchant into the a structure due to the capillary forces. An example of the exceptional selectivity of this technique is shown in Fig. 3. A 3D pattern consisting of uniformly distributed (interval 0.6 μm) single-shot damage spots was recorded in the bulk of silica sample (Fig. 3 (a)). Subsequently, the structure was developed in 5 % HF solution. The measured etching rate of the undamaged Heraus glass in 5 % HF solution is about 50 nm/min, thus only 20 μm of glass can be dissolved in 7 hours. During the same time, the entire length of the recorded 80 μm long spiral was developed as is illustrated in Fig. 3 (b).

Microstructuring of rubber

Finally, we demonstrate reversible femtosecond laser microstructuring in synthetic rubber polymer (cis1,4-polybutadiene (PB)). In this material visco-elastic relaxation of the optically damaged region is responsible for the recovery of optical transmission illustrated in Fig. 4. The recovery time (typically 10^2-10^4 ms) can be varied by changing the pulse energy. Multi-shot induced damage recovers on a much longer scale of 10^1-10^2 s. It was found that the doping of PB by 4%wt. of pentazadiene ([4-NO_2]-Phenyly-N=N-N(C_3H_7)-N=N-Phenyly-[4-NO_2]) reduces the

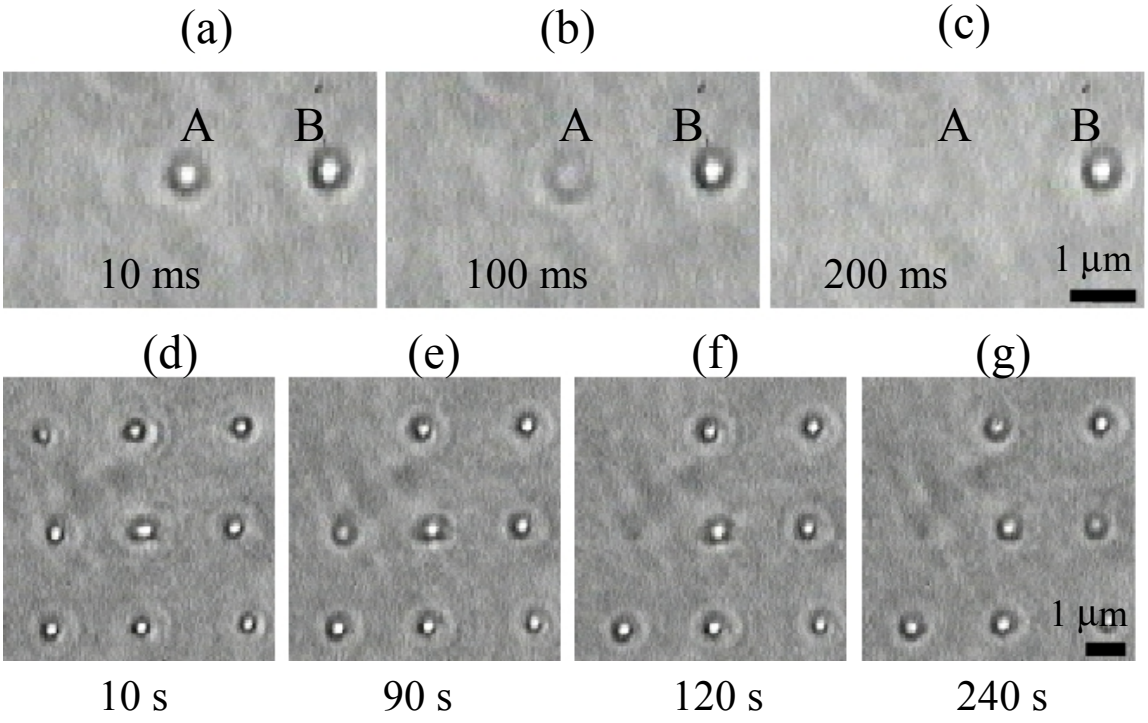

Figure 4. Recovery of the optical transmission in a fs-irradiated PB film. (a) Optical damage resulted from a single 15 nJ pulse at the point *A,* and 5 pulses of the same intensity at the point *B*. The LIDT was estimated as 7.3 ± 0.5 nJ/pulse at 795 nm. The pulse duration in the focus was about 350 fs, focal depth 10 μm, (b) damage resulting from 1000 pulses with 13.1 nJ/pulse energy (LIDT of 6 nJ for 100 pulses was estimated). The time of the snapshots is indicated in the images.

threshold of light-induced damage by 20%. This is explained by photo-induced (homolytic) cleavage of pentazadiene bonds and formation of gaseous N_2, which facilitates material failure at the irradiated spot. The recovery of optical transmission can be applied for the optical memory, photonic crystal, and micro-mechanical applications. The underlying mechanism of the phenomenon can be understood in terms of anelastic α- and β-relaxation (polymer backbone and chains/coils relaxation, respectively).

CONCLUSIONS

Femtosecond laser microfabrication, implemented as *direct laser writing,* has been successfully used to obtain channel structures in silica-based and polymer glasses. This initial laser processing step has been successfully supplemented by the chemical development step in which the laser irradiated patterns are wet-etched by a carefully chosen etchant. Using these methods, channels with 5-50 μm diameter and typical aspect ratio of 10 can be fabricated in silica. In PMMA, channels as long as few-hundreds of micrometers, and diameters of the hollow parts as small as few micrometers have been fabricated this way. These structures are prospective for microfluidic applications.

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