# Three-dimensional microfabrication inside photosensitive glasses by femtosecond laser

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Femtosecond laser is used to form three-dimensional (3D) microstructures embedded in FOTURAN, a photosensitive glass. The microstructures are realized using a three steps process including infrared femtosecond exposure, heating process and etching in an ultrasonic solution of hydrofluoric acid in water. The experiments were carried out using a specially designed ultrafast laser micromachining station, which included a femtosecond laser (170fs, 800nm, 1 mJ/pulse at repetition rate of 1kHz), a beam shaping apparatus and a 3D fully automated positioning system. The photosensitization mechanism involves the generation of a photoelectron due to the absorption of six photons, which then neutralizes the silver ions thus forming crystallized areas upon heat treatment. Efficiency of the fabrication process is discussed in terms of the various laser and etching fabrication parameters. An example of the fabrication of a 3D microfluidic system for biomedical applications is presented.

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## 1. Introduction

Photosensitive glasses, which were developed at Corning Glass Works in 1947 [1], have very interesting properties for of the fabrication of microsystems, such as a high Young's modulus, a low absorption coefficient in the visible wavelengths and a good chemical stability and biocompatibility. They are now used in many technological applications, including GEM-Type detectors [2], hydrodynamic microelectrochemical reactor for voltametric sensing of chemical species [3], nanotube-based field emission flat panel display [4], ultra-long glass tips for atomic force microscopy [5] and miniaturised satellites [6]. In the past, FOTURAN, and other photosensitive glasses, has been mostly process using either Hg lamp [5,7] and UV laser [8,9]. Since the FOTURAN's transmissivity is low for UV photons, these methods permit to fabricate microstructures only near the surface of the sample. To fabricate three-dimensional microstructures deep under the surface, Kondo et al [10] and Cheng et al [11] used, respectively, the 2$^{nd}$ harmonic of femtosecond laser and an infrared femtosecond laser for which the FOTURAN is transparent except at the focussing point where multiphoton absorption occurs leading to a local phase transformation in the glass. With this process, embedded deep 3D structures such as Y or U shaped inter channels have been produced [10,11].

FOTURAN, manufactured by Schott glass Co, is a lithium aluminosilicate photosensitive glass doped with some silver, cerium, and antimony atoms. The main idea behind the processing of FOTURAN is to light induce a local phase change from amorphous to crystalline in the glass, yielding to a significant increase in the etching rate of the irradiated regions thus creating 3-D microstructures. Irradiation of the glass by a laser leads to the photoreduction of $Ag^+$ ions to form Ag which then act as nucleation centers during the heat treatment, thus inducing the growth of the crystalline phase of lithium metasilicate of 1 to 10 μm around the silver clusters. Since the crystalline phase of FOTURAN is brown and the amorphous phase is still clear, this heat treatment leads to the formation of a latent image.

The crystalline areas are removed by using a dilute solution of hydrofluoric acid (HF) in an ultrasonic bath at room temperature. The 10% HF solution could break the tight binding of Si and O atoms in $SiO_2$ compound which form the main part of the glass. Even if both crystalline and amorphous phases are etched by this solution, the crystalline regions are etched faster by a factor of 20 to 50, resulting in the formation of embedded microstructures.

In this paper, we used the femtosecond laser to fabricate 3-D microstructures in FOTURAN. A systematic study of the relation between the size of the microstructures and the laser parameters and a discussion on the basic mechanism of photosensitization of FOTURAN are presented. A 3-D microstructure including channels with varying controlled diameter for microfluidic applications is presented.

## 2. Experimental setup

The experiments were carried out using a specially designed ultrafast laser micromachining station, which included a femtosecond laser (Spectra Physics, 170fs, 800nm, 1 mJ/pulse at repetition rate of 1kHz), systems for the delivery, high-precision focusing and spatial-temporal control of the laser beam, and a fully automated and programmed system for the precise target positioning over a prescribed 3D trajectory. The beam was focused by a Mitutoyo NIR 5X objective with the focal length of 4 cm and the laser fluence was controlled by changing the radiation energy with the help of a fine and coarse attenuators. To control the process, the sample was mounted on a x-y-z translation stage with submicron precision of the target positioning (detailed description of the laser microfabrication system is given in Ref. [12]). To correctly estimate absolute values of the laser fluence, we measured in air the beam waist (spot diameter corresponding to $1/e^2$ of the radiation intensity) by the "knife edge" technique as $\omega_0$=4.1±0.2 µm [13] in the focal plane of the focusing objective. Note that our spot radius differs substantially from *Sugioka et al* [11] ($\omega_0$=13µm) and *Kim et al* [14] ($\omega_0$=39µm).

All samples were heated in a quartz tube Thermolyne 21100 Furnace which is controlled to a 3ºC accuracy by an Omega CN4420 model heat controller. The temperature variation is essentially the same as the one published by many authors [7,8,11]: 4ºC/min, and kept at 500ºC during one hour followed by a further heating step at 2ºC/min and kept at 605ºC for one hour. The samples are then cooled down at a rate of 5ºC/min.

## 3. Optical characterization of FOTURAN

Figure 1 shows that the transmissivity of a 2 mm thick FOTURAN sample at the laser wavelength of 800 nm, is higher than 90% which is essentially due to the reflection losses at surfaces. While the FOTURAN is transparent to a femtosecond laser, multiphoton absorption arises at the focusing point into the material, yielding to the formation a 3-D image. Note that by comparison, at a wavelength of 248 nm for the KrF excimer laser, the transmissivity is less than 0.2%, yielding to a process with a predominant surface etching.

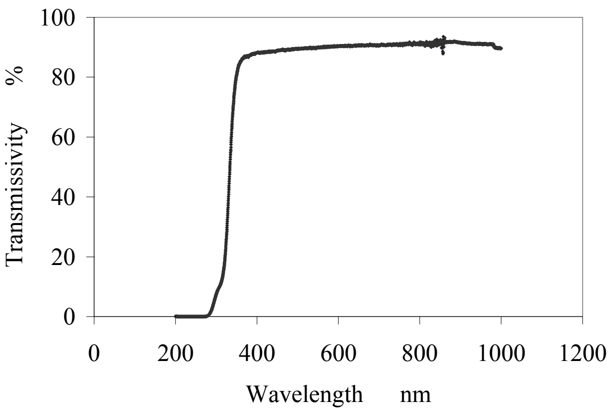


**Fig. 1** Spectral transmissivity of a 2 mm thick FOTURAN sample.

A «pure» $SiO_2$ structure has an optical bandgap larger than 8 eV [15]. The presence of other components ($LiO_2$, $K_2O$, $Al_2O_3$, ..) and dopants (Ag, Ce, …) in the FOTURAN incorporates important defect bands into the materials, strongly affecting the optical transmissivity. The absorbance calculated from the transmission spectrum was used to determine the position of the predominant defect band $E_D$. Figure 2 shows that by using the usual Tauc's expression [16]

$$EK(E) \propto (E - E_D)^2 \quad (1)$$

for amorphous solids describing the absorption coefficient $K(E)$ , as a function of the photon energy $E=\hbar\omega$, the defect band is found to be located at $E_D=3.6 \pm 0.3$ *eV* for FOTURAN.

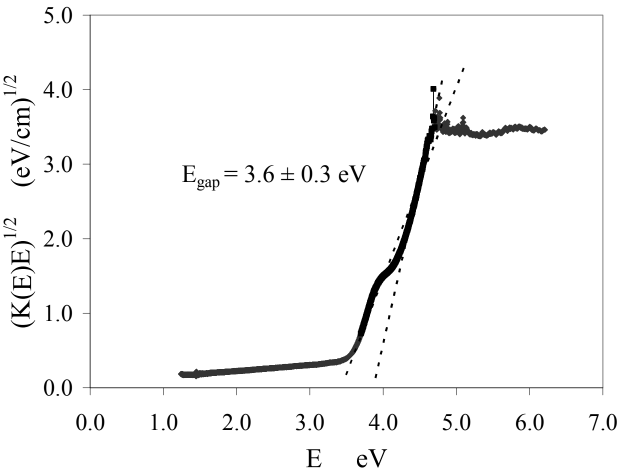


**Fig. 2** Determination of the predominant defect band in FOTURAN by the Tauc's model.

## 4. Photosensitization mechanism

The photosensitization mechanism of FOTURAN with femtosecond laser has not been clearly described. To determine the quantity of photons required to produce multiphoton absorption in these materials, we used, as *Fuqua et al* [8], the hypothesis that there exists a critical dose, $D_c$, above which photostructurable glass forms a latent image, and below which, no image is formed. The critical dose is the dose required to create a density of nuclei large enough to result in an interconnected network of crystallites. For N pulses, $D_c$ is related to a critical fluence $F_c$ above which a photostructurable glass forms a latent image. The relation between the critical fluence and the critical dose is strongly dependant of the number of photons m involved in the multiphoton absorption. In the model developed by *Fuqua et al*, $D_c$ is a constant which merely depends on material composition and process parameters, and can be written as:

$$D_c = F_c^m N \quad (2)$$

Figure 3 presents experimental results of $F_c$ as a function of N, as determined by optical microscopy on samples after photosensitization and baking steps. Graphically, it is found that m= 6 ± 1 photons are required to obtain photosensitization which compared exactly with *Masuda et al* [17] who obtained m=6. Note that *Kim et al* [14] who found m=3, used a different methodology consisting of measuring the transmitted power during the laser photosensitization process. These results suggest the existence of a two-step photosensitization mechanism of FOTURAN [18,19]. First, the femtosecond laser pulse irradiates the photosensitive glass by exciting electrons from the valence band to a defect band located at approximately 3.6 ± 0.3 eV. Since the 800nm photons correspond to 1.55 eV, this excitation requires at least three-photons. This intermediate state created by the presence of impurities in the glass has an unknown lifetime.

Second, at least three others photons are necessary to excite the electrons from the defect band to the conduction band. The total process involves at least six photons in two steps of three photons.

The values of $F_c$ and $D_c$ are significantly higher than those measured by Masuda et al [17] in experiments performed with a larger beam radius of 13µm. A similar phenomena was noted by Martin et al [20] who measured an increase in the fs laser ablation threshold in glass as the beam spot size decreased from 400 to 20 µm. The reason for our larger $F_c$ and $D_c$ values is actually not clear but might be related, as proposed by Martin et al [20], to a lower probability to hit an absorption site as the beam spot size gets lower. In this case a larger fluence would be required to obtain a photosensitisation. A more systematic work is needed to clarify this phenomena.

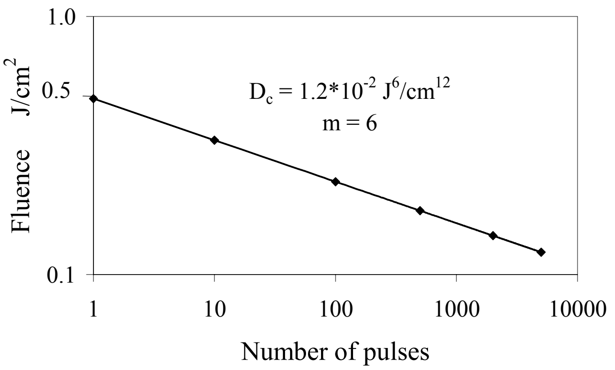


**Fig. 3** Critical fluence as a function of the number of pulses.

Figure 4 shows the absorbance increase as a function of wavelength for photosensitized samples. An absorption increase is observed around 360 nm, which corresponds to the presence of non-bridging oxygen [21]. The wavelength independence of the absorbance increase as a function of laser fluence suggest than the photosensitization mechanism is independent of laser fluence. No significant increase is observed around 315 nm, which corresponds to the presence of $Ce^{3+}$. In agreement with Kondo et al [19,21], we conclude that $Ce^{3+}$ does not seem to play any role in the photoreduction of silver ions present in the photosensitive glass irradiated by a femtosecond laser.

In summary, the photosensitization mechanism in FOTURAN by femtosecond laser pulses at 800 nm is the result of an instantaneous absorption of three photons by non-bridging oxygen near silver ions. An electron is excited from the valence band to a metastable defect state with an energy of 3.6±0.3 eV. Another three photons absorption permits the excitation of an electron from the defect state to the conduction band, which then yields to the neutralization a silver ion.

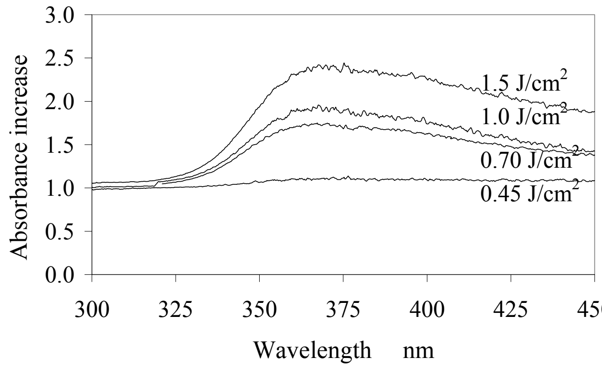


**Fig. 4** Absorbance increase in the photosensitive glass after exposure to the femtosecond laser at 800 nm at various fluences.

## 5. Crystallization and etching parameters

To control the 3D microstructuring process of photosensitive glasses, it is important to determine the effect of the laser parameters (laser fluence and speed) on the crystallized area. Figure 5 presents the depth (d in the y direction) and width (w in the x direction) of the lines written in the z direction by a femtosecond laser at different fluences. All samples were cut with a diamond edge and observed using scanning electron microscopy (SEM). Crystallization depth is plotted as a function of laser fluence for the speed v=70 µm/s, which corresponds approximately to an overlap of 50 pulses. We note a crystallization threshold between 0.3 and 0.4 J/cm$^2$ which is in agreement with the photosensitization threshold found in Fig 3 for N=50 pulses. Note that the width of the lines is almost independent of the laser parameters for fluences >0.5 J/cm$^2$ [22]. The elliptic shape of the crystallized area is due to the absorption profile of a gaussian beam inside the glass.

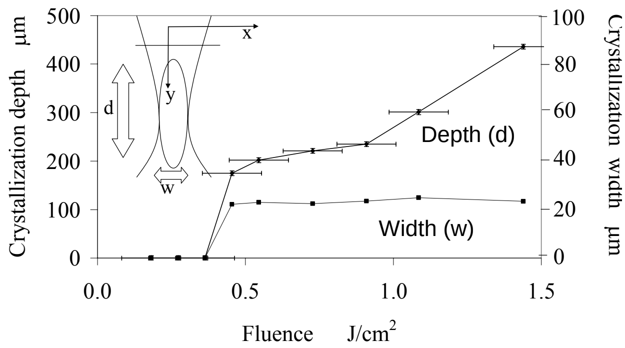


**Fig. 5** Crystallization depth and width as a function of laser fluence at a writing speed of 70 µm/s

In Figure 5, the crystallized depth increases rapidly at fluences greater than 0.9 J/cm$^2$. As is it known, FOTURAN is a non-linear optical material where the refraction index

$$n = n_0 + n_2 I \quad (3)$$

depends on the light intensity I. For $n_2$ positive and at high fluences, self-focusing occurs [23] as a consequence of the wavefront velocity of the beam center being lower than the velocity at the borders. The pulsed laser beam propagation in a non-linear media could yield to the formation of a long filamentation zone with a diameter of a few microns. This phenomenon, which explains the rapid crystallized depth increased at F>0.9 J/cm$^2$, could be used to rapidly produce holes through a thick photosensitive glass.

Figure 6 shows the crystallized line depth as a function of the writing speed. As the speed is lower, more pulses overlap, leading to more absorbed photons and an increase in the crystallized depth.

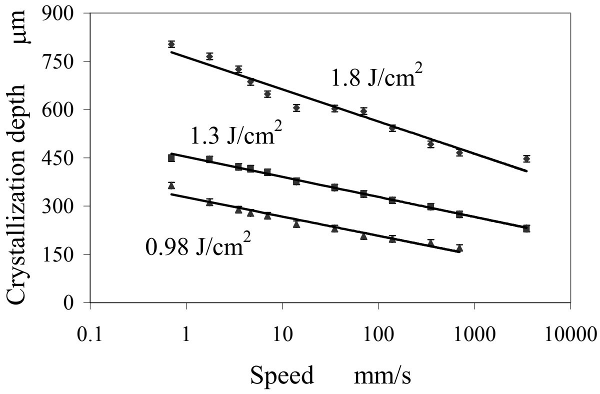


**Fig. 6** Crystallization depth as a function of speed at various laser fluences

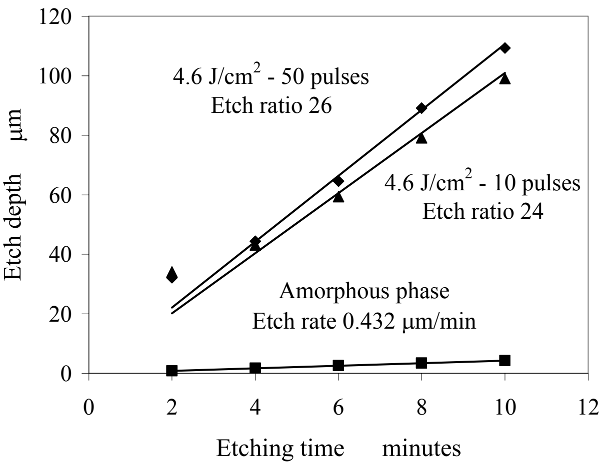


**Fig. 7** Etch depth and etch ratio determination

After the heat treatment, all samples are etched in a 10% HF dilute solution. Figure 7 shows the etched depth for both a non-photosensitized material and the photosensitized one on the surface in different conditions. The etch rate is 0.43 µm/min for the amorphous regions and approximately 11 µm/min for the crystallized regions, almost independent of the processing conditions. The etch ratio between the crystalline and amorphous regions is approximately 25. Note that these results are only valid for «surface» processes and when microchannels are fabricated, the etching rate is expected to be different, as the movement of the liquid is limited in small dimensions.

## 7. Fabrication of three-dimensional microstructures

Figure 8 shows a typical microstructure that is essentially impossible to make by other means. It consist of two reservoirs 500 x 500 x 60 µm$^3$ linked by a 2 mm long microchannel with a diameter varying from 170 µm to 20 µm at the central point. The microchannels of this U-shape structure are embedded 100 µm below the surface. The main purpose of this structure is to confine optically bacteria with a typical size of 5 µm into the microchannel and observe them as they cross one at a time the tight central point of the channel. This microstructure was performed with a 5X objective and the overall etching process took four hours. As seen in Figure 8(a), the glass surface is not perfectly flat due probably to a non-uniform etch of the amorphous phase; that surface would probably required a polishing step. Finally, we noted that the cross-section of the channel is higher than the original crystallized regions probably due to the additional undesirable etching of the amorphous phase. This fact was actually used to obtain a microchannel with a variable diameter.

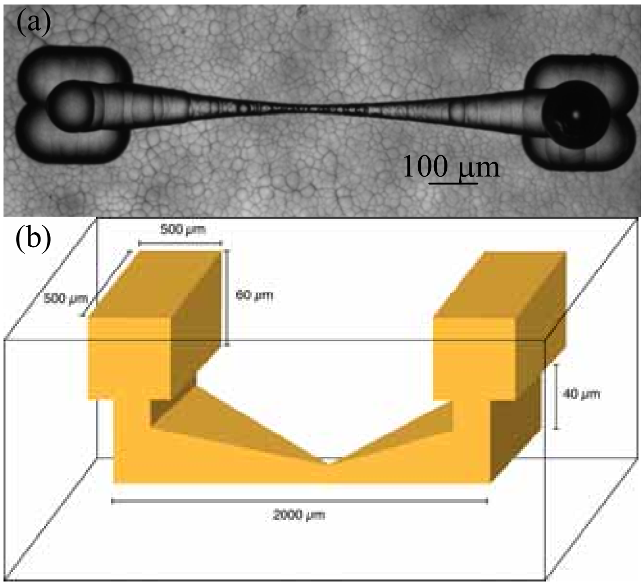


**Fig. 8 (a)** Top View of a U-shape channel embedded 100 µm below the surface **(b)** 3-D sketch of the microsystem for bacteria observation.

## 8. Conclusions

We have fabricated 3D microstructures embedded in a photosensitive glass by using a femtosecond laser photosensitization process followed by heat treatment and chemical etching in an HF solution. Investigation of the transmissivity spectra and defect band determination led to the conclusion that the photochemical reaction mainly arises from the photoelectrons generated by an excitation of an electron of non-bridging oxygen through intermediate states using six photons in total. With this high-order multiphoton process, the crystallized area inside the photosensitive glass could be reduced and very deep structures can be fabricated. We have also shown that the effect of self-focusing and filamentation phenomena take place at high fluences which could be used to rapidly make deep holes. As an example, we fabricated a U-shape microchannel with varying cross-sections by controlling the laser fluence and speed. Applications of these structures to biomedical devices are under development.

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