Femtosecond laser three-dimensional microstructuring inside photosensitive glasses

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ABSTRACT

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 (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. 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.

Keywords: Femtosecond laser, 3D microfabrication, photosensitive glass, microchannel.

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 voltammetric sensing of chemical species[3], nanotube-based field emission flat panel display[4], ultra-long glass tips for atomic force microscopy[5] and nanosatellites[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 transmittivity is low for UV photons, these methods permit to fabricate microstructures only on the «surface» of the sample. To fabricate real 3-D microstructures, Kondo et al[10] and Cheng et al[11] used 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].

In this paper, we used the femtoseconde 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 three-dimensional microstructure including channels with varying controlled diameter for microfluidic applications is presented.

2. PRINCIPLES OF THE MICROSTRUCTURING

FOTURAN, manufactured by Schott glass Co, is a lithium aluminosilicate photosensitive glass doped with some silver, cerium, and antimony. The main idea behind processing of FOTURAN is to light induce a lo-

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cal phase change from amorphous to crystalline in the glass, yielding to a significant increase of the etching rate of the irradiated regions thus creating three-dimensional microstructures. The process requires the following three steps

First step : Photosensitization: Irradiation of the glass by the laser leads to the photoreduction of Ag^+ ions to form Ag which will act as nucleation centers during the heat treatment. After this first step, there is an invisible image, called latent image, which will appear as a brownish image after the heat treatment. While the process for UV source has been detailed by many authors[6,7] as the results of the formation of an unstable Ce^{3+} ions which will then loose one electron leading to the photoreduction of Ag^+ ions, the exact mechanism for infrared femtosecond laser is not well understood. For instance, it has been demonstrated that photoreduction of silver ions occurs in a photosensitive glass even without the presence of Ce^{3+} ions[12]. Kondo et al[13] proposed recently that the photoreduction of Ag^+ ions occurs near non-bridging oxygen (NBO) after a multiphoton absorption.

Second step : Heat Treatment: Samples are heated at a rate of 4ºC/min, and kept at 500ºC during one hour. During this annealing, Ag atoms formed during the photosensitization step agglomerate to form bigger nuclei. Then the temperature is increased at a rate of 2ºC/min and kept at 605ºC during one hour, thus inducing the growth of the crystalline phase of lithium metasilicate around the silver clusters which act as crystallization nuclei. After the samples are cooled down, the crystals of Li_2SiO_3 have a diameter between 1 and 10 μm. After this heat treatment, the latent image is developed: the crystalline phase of Foturan is brown while the amorphous phase is still clear.

Third step: Etching: 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.

3. 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 two attenuation "roulettes" (fine and coarse). 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. [14]). To correctly estimate absolute values of the laser fluence, we measured the beam waist (diameter of the spot corresponding to $1/e^2$ decrease of the radiation intensity) by the "knife edge" technique as $d=4.1\pm0.2$ μm[15] in the focal plane of the focusing objective.

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.

4. OPTICAL CHARACTERIZATION OF FOTURAN

Figure 1 shows that the transmittivity of a 2 mm thick FOTURAN sample at the laser wavelength of 800 nm, is higher than 90% which is essentially due to the loss in surface reflection. 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 wavelenght of 248 nm for the KrF excimer laser, the transmittivity is less than 0.2%, yielding to a process with a predominant surface etching.

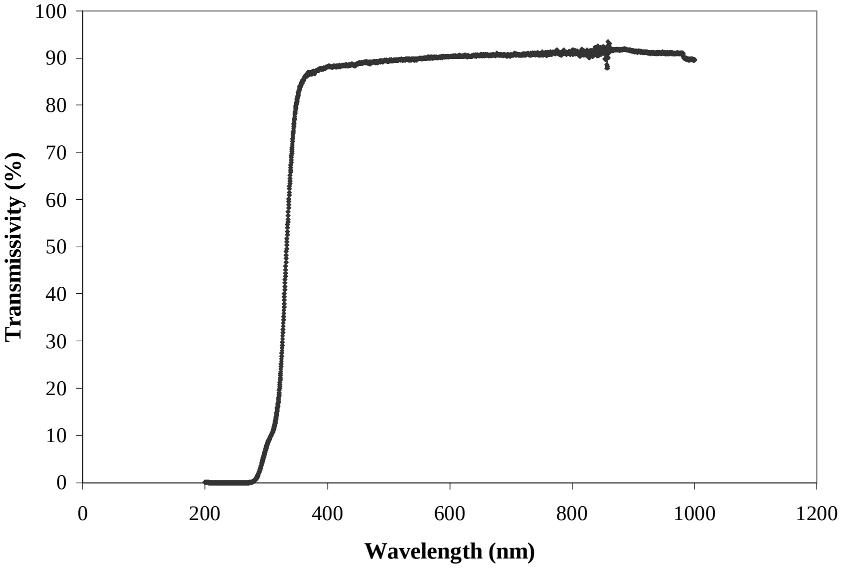

Figure 1 : Spectral transmittivity of a 2 mm thick FOTURAN sample

A «pure» SiO_2 structure has an optical bandgap larger than 8 eV. 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 transmittivity. The absorbance calculated from the transmission spectrum was used to determine the position of the predominant defect band E_{def}. Figure 2 shows that by using the usual Tauc's expression $\omega K(\omega) \propto \left(E - E_{def}\right)^2$ for amorphous solids describing the absorption coefficient $K(\omega)$, as a function of the photon energy $E=\hbar\omega$, the defect band is found to be located at 3.6 ± 0.3 eV for FOTURAN.

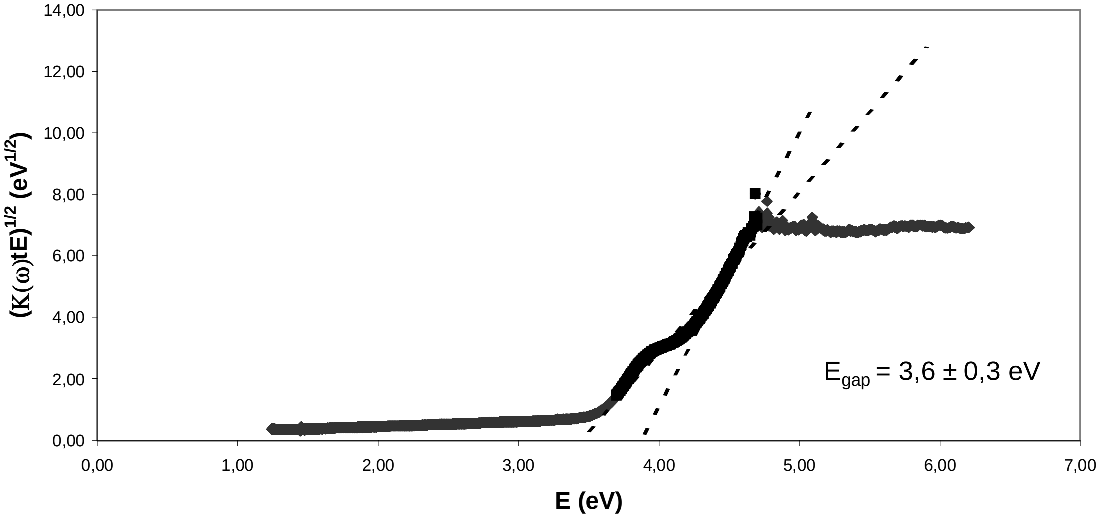

Figure 2 : Determination of the predominant defect band in FOTURAN by the Tauc's model

5. PHOTOSENSITIZATION MECHANISM

The photosensitization mechanism of FOTURAN with femtosecond laser has not been clearly determined. 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 below :

$$D_c = F_c^m N \tag{1}$$

Figure 3 presents experimental results of D_c as a function of N, as determined by optical microscopy on samples after photosensitization and baking steps Graphically, it is found that m= 7 ± 1 photons are required to obtain photosensitization which compared quite favourably with *Masuda et al*[16] who obtained m=6. Note that *Kim et al*[17] 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.

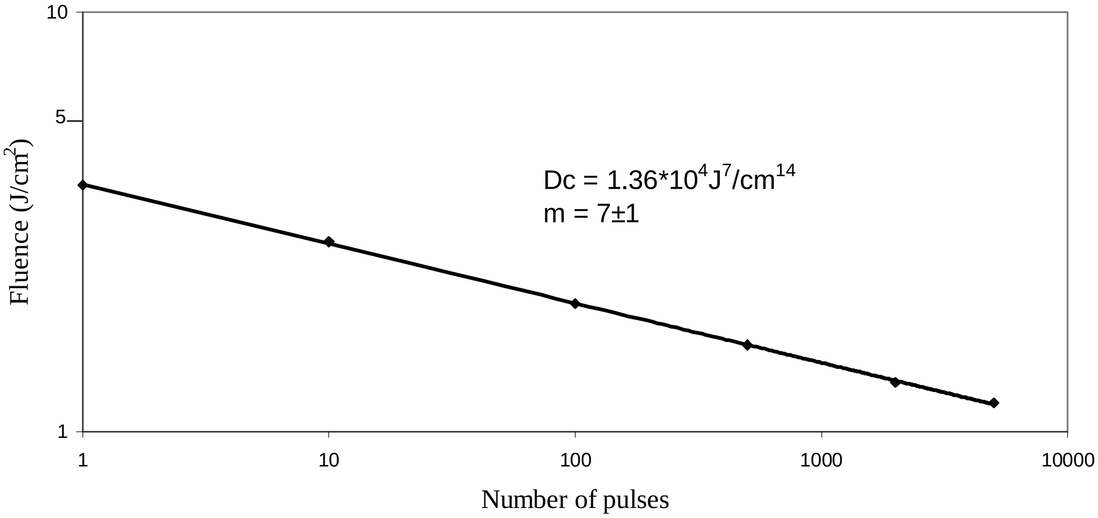

Figure 3 : Critical fluences as a function of the number of pulses

6. 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, speed) on the crystallized area. Figure 4 and 5 present the depth and the width of lines written by a femtosecond laser at different fluences and writing speeds. All samples were cut with a diamond edge and observed using scanning electron microscopy (SEM). On Figure 4.a, crystal depth (i.e. the crystal length parallel to the direction of laser propagation) is plotted as a function of laser fluence for the speed v= 70 μm/s . We note a crystallization threshold between 2 and 2.5 J/cm^2 which is in agreement with the photosensitization threshold found in Fig 3 for N= 50 pulses (estimated from v, d and the repetition rate). Note that the width given in Fig 5 is almost independent of the laser parameters.

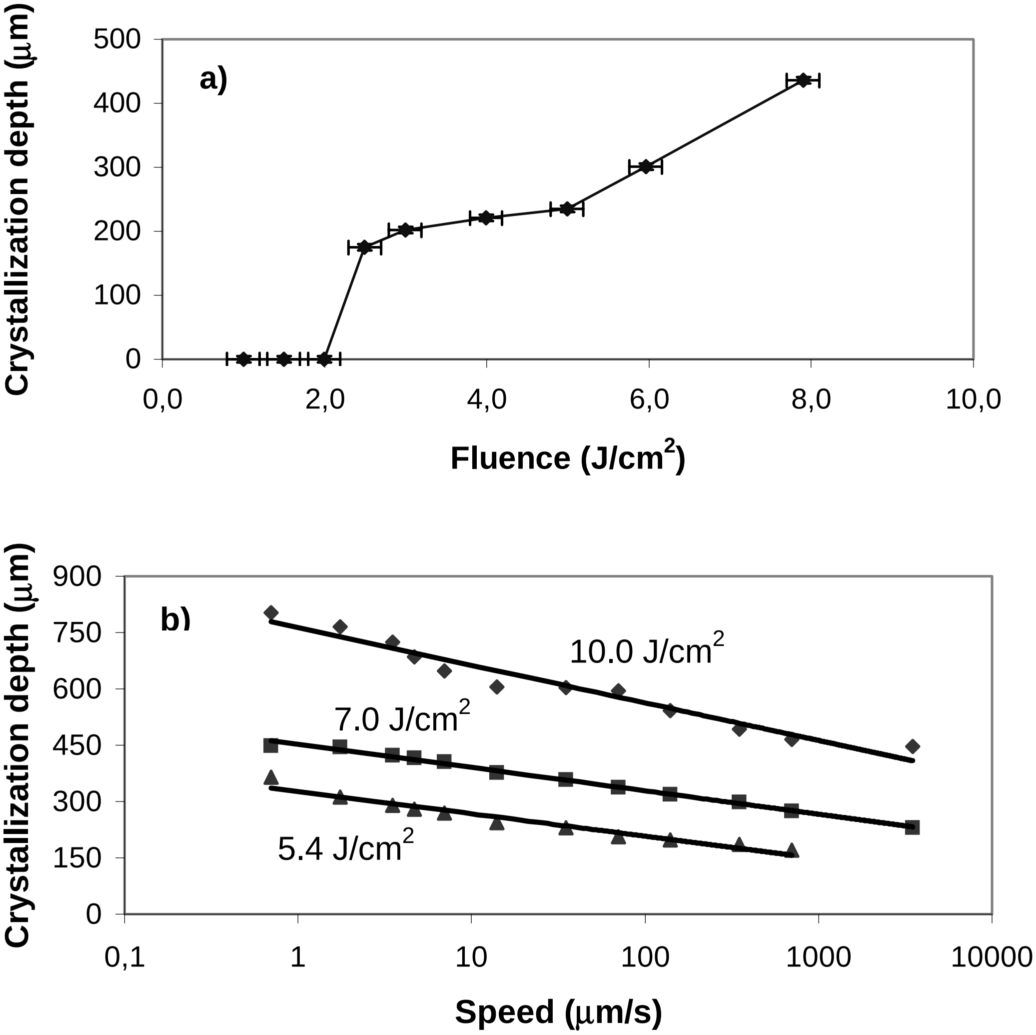

Figure 4 : Crystallization depth as a function of (a) laser fluence at a writing speed of 70 μm/s and (b) speed at various fluences

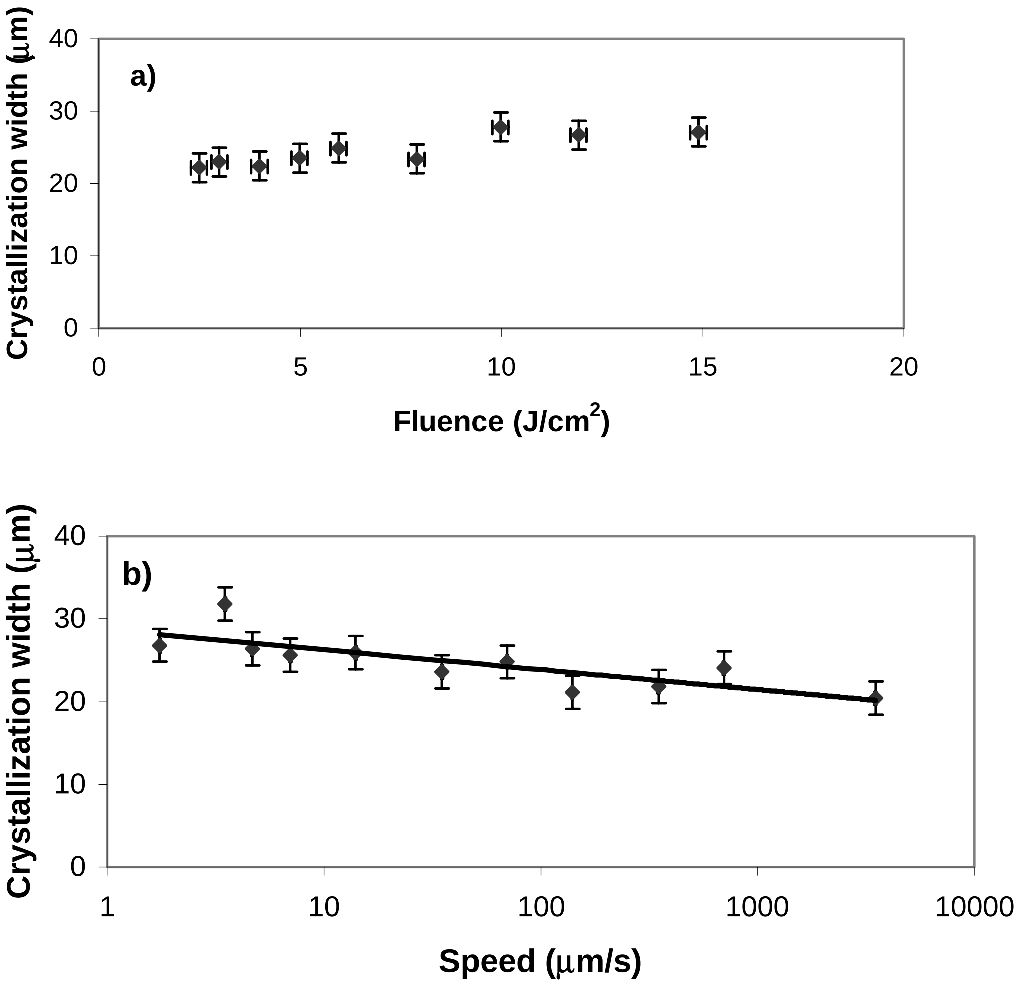

Figure 5 : Crystallization width as a function of (a) laser fluence at 70 μm/s and (b) speed at fluence of 10 J/cm^2

FOTURAN is a non-linear optical material where the refraction index $n=n_0+n_2I$ depends on the light intensity I. For n_2 positive and at high fluences, self-focusing occurs[20] as a consequence of the wavefront velocity of the beam centre 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 thickness of a few microns. Figure 6 shows an illustration of this phenomenon in FOTURAN processed at two different laser fluences and writing speeds. The width of the line (a) is 27 μm and the depth is 364 μm and for line (b) the width is 29 μm and the depth is 170 μm. This phenomenon could be used to rapidly produce holes through a thick photosensitive glass.

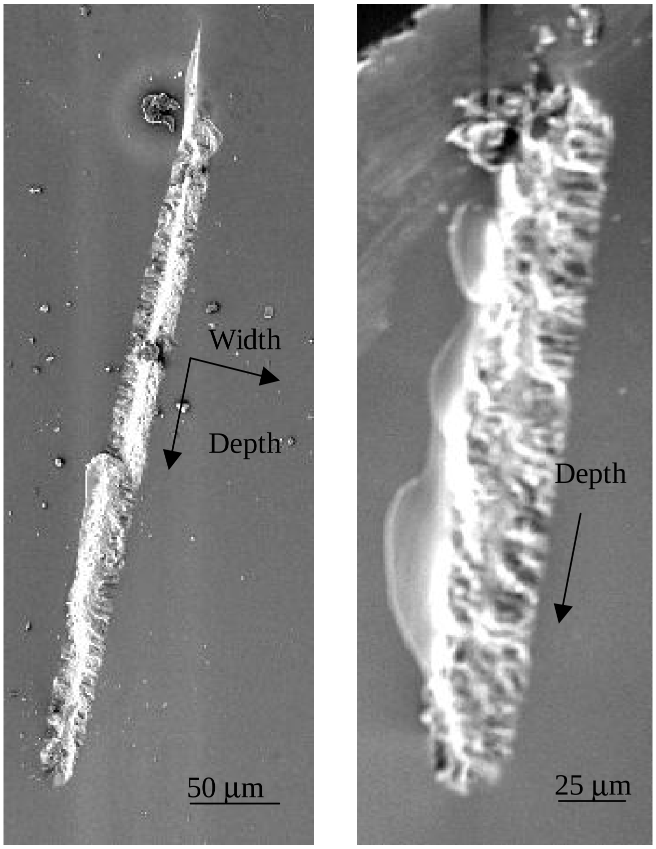

Figure 6 : Transversal view of the crystallization area for (a) 5.4 J/cm^2 and 0.7 µm/s and (b) 5.4 J/cm^2 and 3500 µm/s

After the heat treatment, all samples are etch 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.

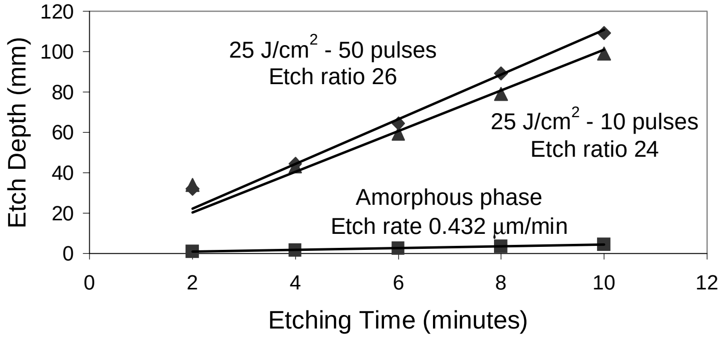

Figure 7 : Etch depth and etch ratio determination

7. FABRICATION OF THREE-DIMENSIONAL MICROSTRUCTURES

Figure 8 shows a typical microstructures 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 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 optically observe the behavior of bacteria with a typical size of 5 µm and observed them as they cross one at a time the tight central point of the channel. This microstructure was done with a 5X objective and the overall etching process took four hours. As seen on Figure 8(a), the glass surface is not perfectly flat due probably to a non-uniform etch of the amorphous phase and 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.

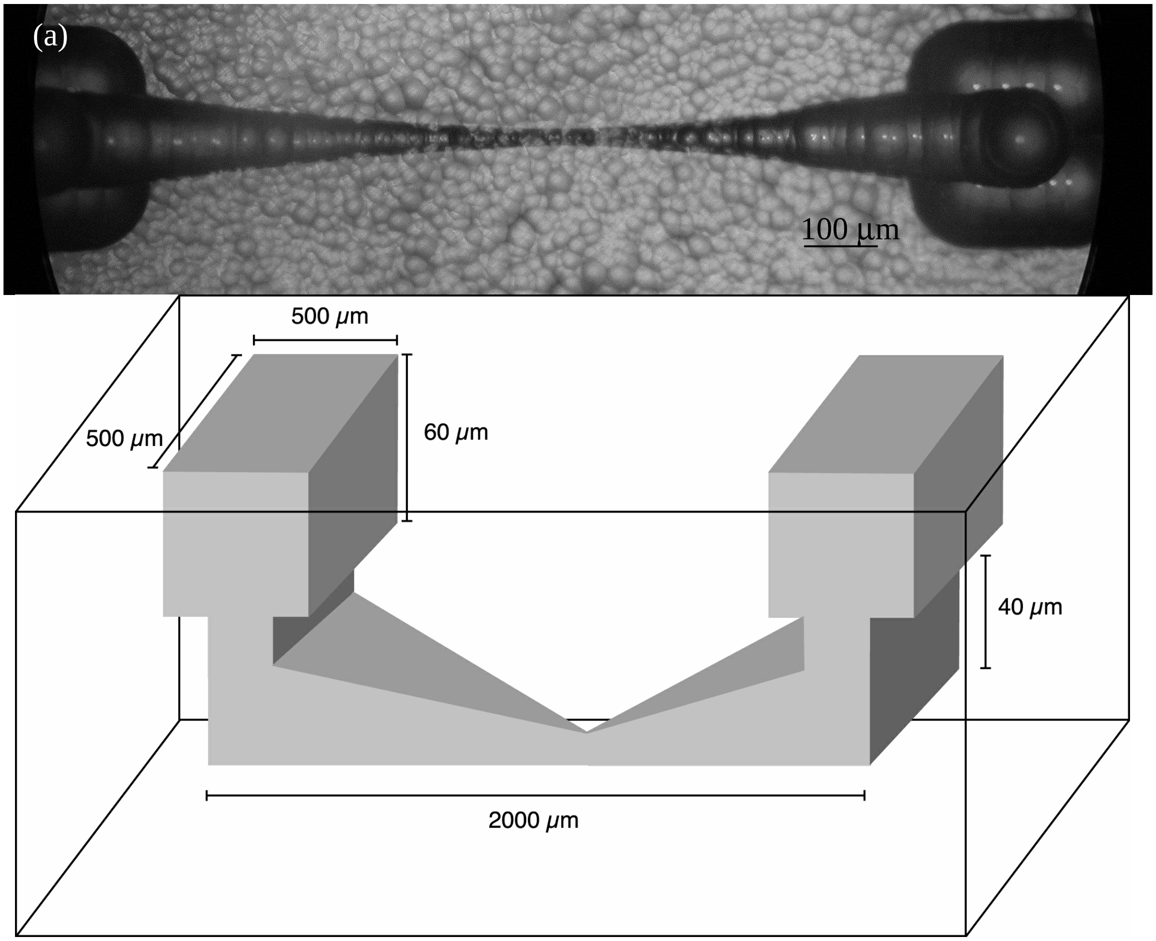

Figure 8 (a): Top view of a U-shape channel embedded 100 µm below the surface
(b) : 3-D sketch of the microsystem for bacteria observation

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 transmittivity spectra and defect band determination led to the conclusion that the photochemical reaction mainly arises from the photoelectrons generated by an excitation through intermediate states using seven 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 fluence which could rapidly make deep holes. As an example, we fabricated a U-shape microchannel with varying cross-sections by controlling the laser fluence and pulse number. Applications of these structures to biomedical devices are under development.

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