Three-dimensional crystallization inside photosensitive glasses by focused femtosecond laser

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Using scanning electron microscopy, we analyze the laser fluence dependence of three-dimensional crystallized areas induced in bulk photosensitive glass (Foturan) by focused femtosecond laser pulses exposition and subsequent heat treatment. For low fluences ($F < 2\ \mathrm{J/cm^2}$), the crystallized area is essentially determined by the energy dose distribution above a critical dose. For higher fluences ($F > 2\ \mathrm{J/cm^2}$), the crystallization length is higher than predicted from the energy distribution due to the filamentation which occurs above a critical fluence $F_{\mathrm{crit}} = 1.4 \pm 0.3\ \mathrm{J/cm^2}$. The filamentation length is found to follow the square root dependence $\sqrt{F - F_{\mathrm{crit}}}$. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2179614]

A femtosecond laser pulse can have an electric-field strength which approaches or exceeds the strength of the electric field that holds valence electrons in a transparent material to their ionic cores.[1] In this regime, the interaction between the laser pulse and the material becomes highly nonlinear. Laser energy can be nonlinearly absorbed by the material, leading to optical breakdown,[2] self-focusing,[3] multiphoton ionization,[4] soft x-ray generation,[5] etc. Photosensitive glasses, which were developed at Corning Glass Works in 1947,[6] have very interesting properties for the fabrication of microsystems, such as a high Young's modulus, a low absorption coefficient in the visible wavelengths, and good chemical stability and biocompatibility. They are now used in many technological applications, including GEM-Type detectors,[7] hydrodynamic microelectrochemical reactor for voltammetric sensing of chemical species,[8] nanotube-based field emission flat panel display,[9] ultralong glass tips for atomic force microscopy,[10] and miniaturized satellites.[11] In the past, Foturan and other photosensitive glasses have been mostly processed using either a Hg lamp[10,12] and ultraviolet (UV) laser.[13,14] Since the Foturan's transmittivity is low for UV photons, these methods permit one to fabricate microstructures only near the surface of the sample. To fabricate real three-dimensional (3D) microstructures, Kondo *et al.*[15,16] and Cheng *et al.*[17–19] used an infrared femtosecond laser for which the Foturan is transparent except at the focusing point where nonlinear multiphoton absorption occurs leading to a local phase transformation in the glass. With this process, deep embedded 3D structures—such as Y- or U-shaped interchannels—have been produced.[15,20]

In this letter, we present a systematic study and an analytical model of the relation between the size of the crystallized areas and the laser fluence. The experiments were carried out using a specially designed ultrafast laser micromachining station, which included a femtosecond laser (Spectra Physics, 170 fs, 800 nm, 1 mJ/pulse at repetition rate of 1 kHz), 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 5× objective with the focal length of 4 cm, and the laser fluence was controlled by changing the radiation energy with two neutral density filter wheels. In order to control the sample positioning, we used a 3D translation stage with submicron precision (detailed description of the laser microfabrication system is given in Ref. 21). To correctly estimate absolute values of the laser fluence, we measured the intensity profile in the incident laser beam by the "knife edge" technique and deduced the $1/e^2$ beam waist in the focal plane as $\omega_0 = 4.1 \pm 0.2\ \mu\mathrm{m}$. The depth of focus of the laser pulse is twice the Rayleigh length ($z_0 = k\omega_0^2/2$) or 130 μm.

When a femtosecond laser is focused inside a transparent media, multiphoton absorption arises around the focal point. By using, the hypothesis (as Fuqua *et al.*[13] did) that there exists a critical dose above which photostructurable glass forms a latent image and below which no image is formed, we have found that 6 ± 1 photons are required to obtain photosensitization,[22] which compares exactly with Masuda *et al.*[20] who obtained a six-photon absorption. Note that Kim *et al.*,[14] who found three-photons absorption, 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.[23,24] First, the femtosecond laser pulse irradiates the photosensitive glass by exciting electrons from the valence band of nonbridging oxygen[25,26] to a defect band located at approximately 3.6 ± 0.3 eV above the valence-band energy.[27] Since the 800 nm 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.[23] Second, at least three others photons are necessary to excite the electrons from the defect band to the conduction band at approximately 8 eV above the valence-band energy.[28] Therefore, the total process involves at least six photons in two steps of three photons. The ejected electron served to reduce Ag^+ ions, which act as a nucleation center for the lithium metasillicate matrix during baking step.[7] The final result of this process, involving fs laser irradiation and heating steps, is the apparition of a visible latent image revealing where the crystallites were formed.

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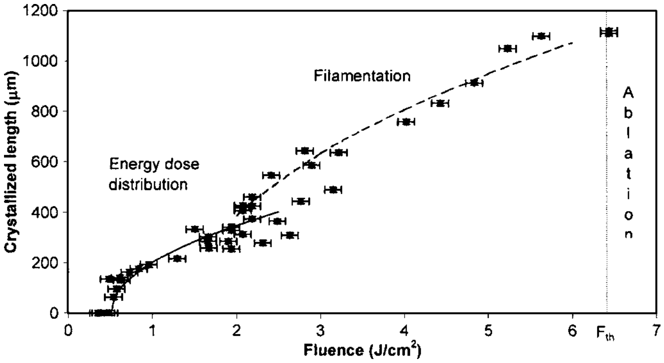

FIG. 1. Crystallization length inside Foturan as a function of the laser fluence at a writing speed of 3.5 mm/s.

All experiments were performed by focusing the laser at approximately 500 μm inside the Foturan and displaced the beam parallel to the surface at a writing speed of 3.5 mm/s, which corresponds to an overlap of approximately one pulse. All samples were then cut in the plane parallel to the beam direction (or perpendicular to the writing direction) revealing the cross section of the irradiated zone that we measured by scanning electron microscopy (SEM). Figure 1 presents the length of lines crystallized by a fs laser at different fluences. The full line represents the dimension predicted by a simple analytical model in which we consider the 3D intensity distribution (I) in the focal plane of a tightly focused laser beam

$$I = \frac{(1-R)I_0}{(1+z^2/z_0^2)} \exp\left[\frac{-2(x^2+y^2)}{\omega_0^2(1+z^2/z_0^2)}\right], \quad (1)$$

where the coordinate origin is at the geometrical centre of the focal point, z denotes the beam propagation direction, ω_0 is the beam waist, $z_0=k\omega_0^2/2$ is the corresponding Rayleigh length, I_0 is the intensity, and λ and k are the wavelength and wave vector, respectively. The optical reflectivity R and refractive index of Foturan at 800 nm are equal to 0.04 and 1.515, respectively. The absorption of the laser pulse along the laser propagation direction is neglected because Foturan is a transparent material at 800 nm (linear absorptivity is $\alpha \cong 0.2\ \mathrm{cm}^{-1}$) and absorption occurred only by multiphoton processes. This intensity distribution is used to calculate the energy dose D which represents an energetic threshold characterizing the necessary energy to structurally alter the bulk transparent material.[13] D is given by the phenomenological expression:[13]

$$D = F^m N, \quad (2)$$

where the laser fluence F is related to the intensity of a laser pulse with a duration τ by $F=I\tau$ and $m=6$ denotes the number of photons needed to get over the energy band gap. Because each laser pulse induces irreversible modification of the absorption, this formula is only applicable to a limited number of laser pulses N. To assure the validity of the analysis, a high writing speed (3.5 mm/s) was chosen in order to limit pulse overlaps which could induce cumulative effects in the irradiated zone. For such a small N, D is experimentally evaluated as $D=1.2\times10^{-2}\ \mathrm{J}^6/\mathrm{cm}^{12}$.[27] To prevent permanent damage inside the glass, small N $(1<N<5000)$ and low fluences $(F<0.5\ \mathrm{J/cm}^2)$ were used to determine D. Note that for very low laser fluences, thousands pulses are needed to induce a photomodification of the glass. The full line in Fig. 1 is the length of the region along the z direction calculated by using Eq. (1), where $I=F/\tau$ is determined by Eq. (2).

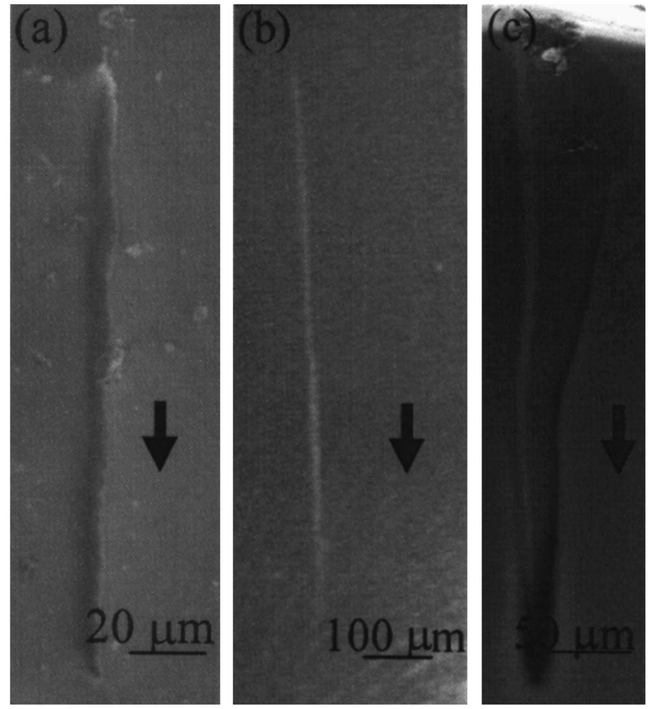

FIG. 2. SEM pictures showing the cross-sections of a crystallized line processed at a fs laser fluence of (a) 0.95 J/cm^2, (b) 4.4 J/cm^2, and (c) 8.5 J/cm^2. The arrows indicate the direction of laser propagation.

For low fluences $(F<2\ \mathrm{J/cm}^2)$, the crystallized area is essentially determined by the energy distribution above a critical dose [Fig. 2(a)]. Since the crystal size varies between 1 and 10 μm,[12] the crystal formation causes little error on the predicted dimensions. For higher fluences $(F>2\ \mathrm{J/cm}^2)$, filamentation occurs and the crystallization length is higher than predicted from the energy distribution [Fig. 2(b)]. Foturan is a nonlinear optical material where the refractive index $n=n_0+n_2I$ depends on the light intensity I. For a positive n_2 and at high fluences, self-focusing occurs[29] as a consequence of the wave front velocity of the beam center being lower than the velocity at the borders. The pulsed laser beam propagation in a nonlinear media could yield the formation of a long filamentation zone with a thickness of a few microns and a length proportional to $\sqrt{F-F_{\mathrm{crit}}}$ where F_{crit} is the critical fluence for filamentation.[30] Figure 3 shows that the length follows that relation with

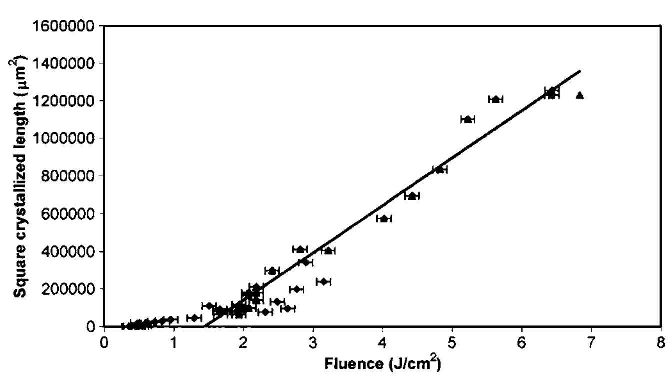

FIG. 3. Square of crystallization length as a function of laser fluence at a writing speed of 3.5 mm/s.

$F_{crit}=1.4\pm0.3$ J/cm^2, which corresponds to the fluence for a zero square root. From the theory of nonlinear optics, the filamentation happens at the critical power P_{crit} given by the phenomenological expression[31]

$$P_{crit}=\frac{3.77\lambda^2}{8\pi n_0 n_2}. \tag{3}$$

By using the z-scan method,[32] the nonlinear refraction index of Foturan was determined as $n_2=(4.3\pm0.7)\times10^{-16}$ cm^2/W, and this value allows one to calculate [with Eq. (3)] a critical fluence of filamentation of 0.8 ± 0.2 J/cm^2 which is quite close to the experimental F_{crit}. Introducing in Fig. 1—a square root dependence between the laser fluence and the crystallization length for $F>2$ J/cm^2 permits one to correctly predict the crystallization dimensions for laser fluences below the ablation threshold of $F_{ablation}=6.3$ J/cm^2. For higher fluence ($F>6.3$ J/cm^2), an explosive mechanism leads to an expansion of the structural modifications out of the focal region into the surrounding material [Fig. 2(c)]. Those very high fluences have no particular interest for 3D crystallization of photosensitive glasses.

In conclusion, the 3D crystallization process in photosensitive glass irradiated by a focused fs laser is mostly determined at low fluences ($F<2$ J/cm^2), by the energy distribution above a critical dose and at higher fluences ($F>2$ J/cm^2), by filamentation whose length follows $\sqrt{F-F_{crit}}$, where $F_{crit}=1.4\pm0.3$ J/cm^2. By controlling the laser parameters, these phenomena could be used to predict and fabricate various forms in photosensitive glasses for diverse applications.

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