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Confocal fluorescence and Raman microscopy of femtosecond laser-modified fused silica

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Abstract

Modified lines were written inside Corning 7940 fused silica with 130 fs laser pulses from an amplified Ti–sapphire laser operating at 800 nm at a repetition rate of 1 kHz. The sample was scanned at 20 μm s^{-1} with laser pulse energies ranging from 1 to 35 μJ, resulting in modified lines with diameters ranging from 8 to 40 μm. Confocal fluorescence and Raman microscopy was used to probe for spatial variations in defect concentration and glass structure across the modified lines. The fluorescence intensity decreased with increasing distance from the line centre, whereas the Raman intensity increased. No significant variations in the concentration of three- and four-membered ring structures were observed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Femtosecond (fs) laser pulses—tightly focused inside a bulk glass—can induce localized refractive index changes of the glass within the focal volume of the laser beam. By scanning the glass with respect to the laser focus, waveguide structures can be fabricated *inside* the glass [1–7]. This technique holds tremendous potential as a fabrication technique for three-dimensional all-optical integrated components with applications in telecommunications as well as in biological and chemical sensors and medical technology.

The mechanism of ultrashort-laser-pulse modification of transparent materials can be divided into several steps [8–12]:

(1) production of initial seed electrons through either non-linear photoionization of free electrons or excitation of impurity defects,
(2) avalanche photoionization,
(3) plasma formation, and
(4) energy transfer from the plasma to the lattice.

Wide-band-gap transparent optical materials cannot linearly absorb visible or near-infrared light because the energy of a single photon is below the energy required to promote an electron across the band gap between the valence and conduction band. However, promotion of electrons from the valence to the conduction band can be achieved by the simultaneous absorption of multiple photons. Following the production of the initial seed electrons in the conduction band through the multiphoton ionization process, the electrons can continue to linearly absorb photons from the laser to move higher up the conduction band. This is known as free carrier absorption. The free electrons gain energy from the laser pulse through electron–phonon–photon collisions, a mechanism known as the Joule heating process, or inverse Bremsstrahlung [11]. When the energy of the free electron builds up to a magnitude greater than the energy of the band gap of the material, the electron can collide with a bound electron in the valence band, transferring the energy to promote the valence band electron to the conduction band. These electrons can continue to absorb photons and/or collide with each other and promote valence band electrons to the conduction band to continue the avalanche ionization process. When a significant number of valence band electrons are ionized through multiphoton ionization and, more significantly, avalanche ionization, a plasma is created in the material.

The final step involves the transfer of the energy from the hot plasma created by the laser pulses to the lattice, resulting in the modified regions in the bulk material. This process is still not well understood, but may involve shock-wave propagation in the material, as proposed by Glezer and Mazur [13], and/or thermal processes, as suggested early on by Davis *et al* [1]. The results of these two steps are physical, chemical, and structural changes, such as densification, index increase, and/or colour centre formation, of the material after exposure to the laser beam.

Previous work on waveguides written in fused silica using a focused fs laser has shown that the intensities of the Raman peaks at 490 and 605 cm^{-1} relative to the total Raman intensity are as much as $5\times$ higher in the modified glass, indicating an enriched population of three- and four-membered ring structures [14–16]. There is also an increase in fluorescence in the modified region due to the formation of non-bridging oxygen hole centres (NBOHC). These features scale with increased irradiance. The increase in three- and four-membered ring structures is consistent with densification inside the modified region [17–20]. This raises an obvious question: if one region has been densified, where did the extra material come from? If a micro-explosion took place, it is conceivable that the modified region would consist of a high-density region surrounding a low-density region or even a void. Such a structure has been deduced from SEM measurements [21] that were performed on the surface that was obtained after cleaving through the modified region.

In the present study we have used confocal Raman microscopy to measure spatial variations across regions modified with fs laser pulses. In order to obtain meaningful data it is necessary to write lines with the fs laser that are substantially larger than the 1–2 μm spatial resolution of our confocal microscope. In this paper we report on fluorescence and Raman profiles across 8–40 μm lines in fused silica created by fs laser pulses.

2. Experimental details

All experiments were performed on Corning 7940 type III silica glass. In figure 1(a) we present a schematic diagram of the experimental set-up used to write the modified lines with the fs laser. Large-diameter modified lines were written in 1 cm^3 fused silica cubes using an amplified Ti–sapphire laser operating at 800 nm with a 100 fs pulse width, and a 1 kHz repetition rate [14, 15]. The beam was focused into the sample with a 6 cm focal length singlet lens resulting in a spot size of $\sim$10 μm. The sample was moved at 20 μm s^{-1}, parallel to the

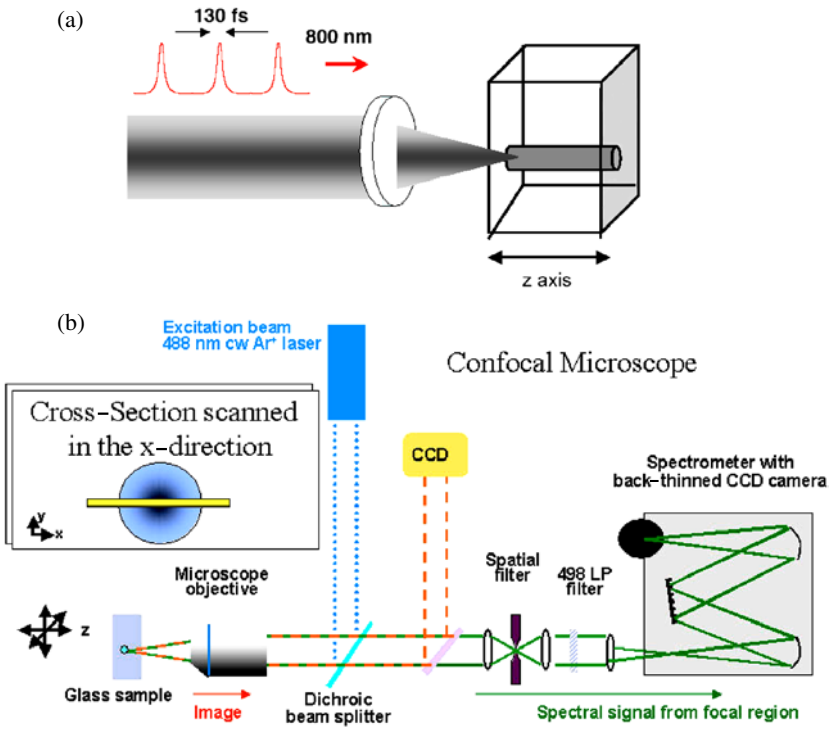

Figure 1. Schematic diagrams of (a) the experimental set-up for writing modified lines in fused silica with fs laser pulses and (b) the scanning confocal microscopy set-up used for fluorescence and Raman spectroscopy.

laser, beam to create the modified lines. Care was taken to ensure that the focal spot never reached the sample surface. A series of lines were written with a separation of 0.5 mm in the x-direction. The laser power was adjusted for each line—from 1 to 35 mW (corresponding to pulse energies from 1 to 35 μJ) in 2 mW increments—using a polarizer and a polarized beam splitter. This range corresponds to the same intensities as were used in earlier studies with smaller spot sizes and lower powers [14, 15]. This allows for direct comparison of the results.

A scanning confocal microscope, schematically shown in figure 1(b), was used to obtain Raman and fluorescence for the lines modified with 9–27 mW laser power. The lines created with less power could not be distinguished from unmodified glass, and the lines created with greater power exhibited excessive damage. Spectral cross-sections were taken for each line with a resolution of 2–4 μm. A 50 mW, 488 nm Ar^+ laser beam was focused onto the sample through a 50× (0.55 NA) achromatic microscope objective lens. A 1/4 m spectrometer with a liquid-nitrogen-cooled CCD detector array was used to collect the fluorescence and Raman spectra, with a 1200 grooves mm^{-1} grating and 30 min acquisition time used for Raman spectroscopy and a 300 grooves mm^{-1} grating and 2 min acquisition time for fluorescence spectroscopy.

3. Results

Figure 2 shows white-light microscope images of the cross-sections of two of the lines written in fused silica. These images, as well as those from other lines, indicate a clear increase in

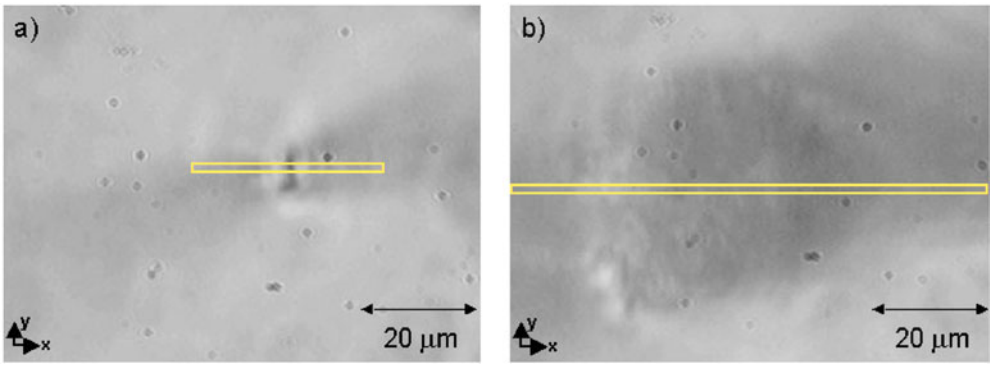

Figure 2. White-light microscope images of the cross-sections of modified lines written in fused silica with a 6 cm focal length lens and (a) 9 μJ and (b) 25 μJ fs laser pulse energy.

the size of the modified region with increasing laser fluence. The diameter of the 9 μJ line is 6–7 μm, slightly smaller than the 10 μm diameter of the laser focus. The diameter of the 25 μJ line is roughly 40 μm. The larger diameter of higher-energy lines indicates that there was sufficient energy for modifications to occur further from focal plane. The white lines in the images indicate the scan range used in the spectroscopic measurements.

Complete Raman and fluorescence spectra were taken for all lines modified with 9–27 μJ fs laser power as a function of distance from the line centre. Typical spectra are shown in figures 3(a) and (b) for locations inside and outside the modified regions. The fluorescence spectra show a broad band centred at 650 nm. For the line written with 9 μJ of fs pulse energy the fluorescence is rather weak and only slightly increased with respect to the unmodified glass. Generally, the fluorescence intensity inside the modified region increases with increasing fs pulse energy. The spectral shape is the same for different locations within the modified region, but the overall intensity increases towards the centre of the modified region.

For the Raman spectra (figures 4(a) and (b)) there is again no change in spectral shape across the modified region, but in this case the overall intensity decreases towards the centre of the modified region. Figure 5 shows the variation of the total fluorescence and Raman intensity across the modified region for the two lines shown in figure 2.

In fused silica the intensity ratio between the 605 cm^{-1} Raman peak, which is due to three-membered ring structures in the silica network, and the total Raman intensity is known to increase with increasing density [17–20]. Since we were particularly interested in variations in density across the modified regions we calculated the intensity of the 605 cm^{-1} peak relative to the total Raman intensity. Similar information can be obtained from the intensity ratios of the 605 and the 800 cm^{-1} peak, since the intensity of the 800 cm^{-1} peak scales with the total intensity. The results are shown in figure 6. No significant variation in the peak ratio is observed across the modified region. To check our methodology we also measured this intensity ratio for lines that were written with the high-NA objective that we used in our earlier studies [14, 15]. For a line written with a pulse energy of 4 μJ and a 50×, 0.55 NA objective, the peak ratio inside the line is about 4× higher than outside the line (figures 7 and 6), consistent with our earlier results. Unfortunately, for this narrow line we cannot obtain a spatial profile of the peak ratio because the width of the line is comparable to the spatial resolution of our confocal Raman probe.

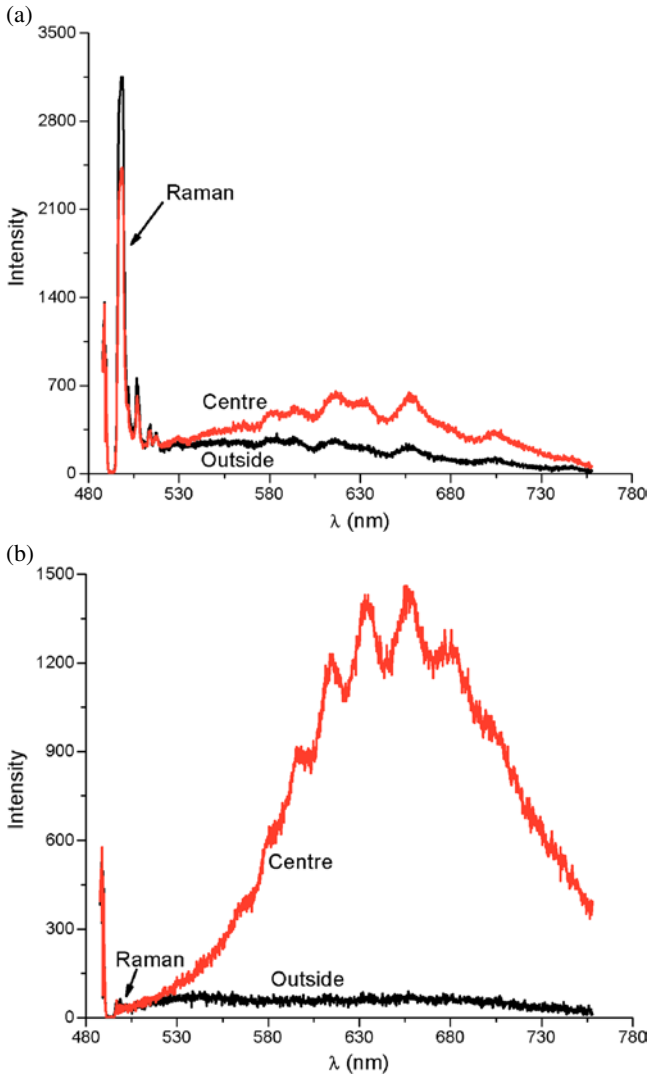

Figure 3. Fluorescence spectra measured from regions inside and outside lines written in fused silica with a 6 cm focal length lens and (a) 9 μJ and (b) 25 μJ fs laser pulse energy. The spectral structure between 550 and 750 nm is an artifact due to the transmission characteristics of the 498 nm long-pass filter.

4. Discussion

Our results show that the 605 cm^{-1}/800 cm^{-1} peak ratio does not vary significantly across the modified region, while the overall Raman and fluorescence intensities change substantially with an increase in the fluorescence, and a decrease in the Raman signal near the centre of each modified line. The fluorescence is due to NBOHC defects, which are formed as a result of bond breaking during fs laser modification [15]. The fluorescence increase towards the line centre indicates an increase in the concentration of NBOHC defects. It should be noted that the limited spatial resolution of the confocal microscope (2 μm) prevents us from accurately

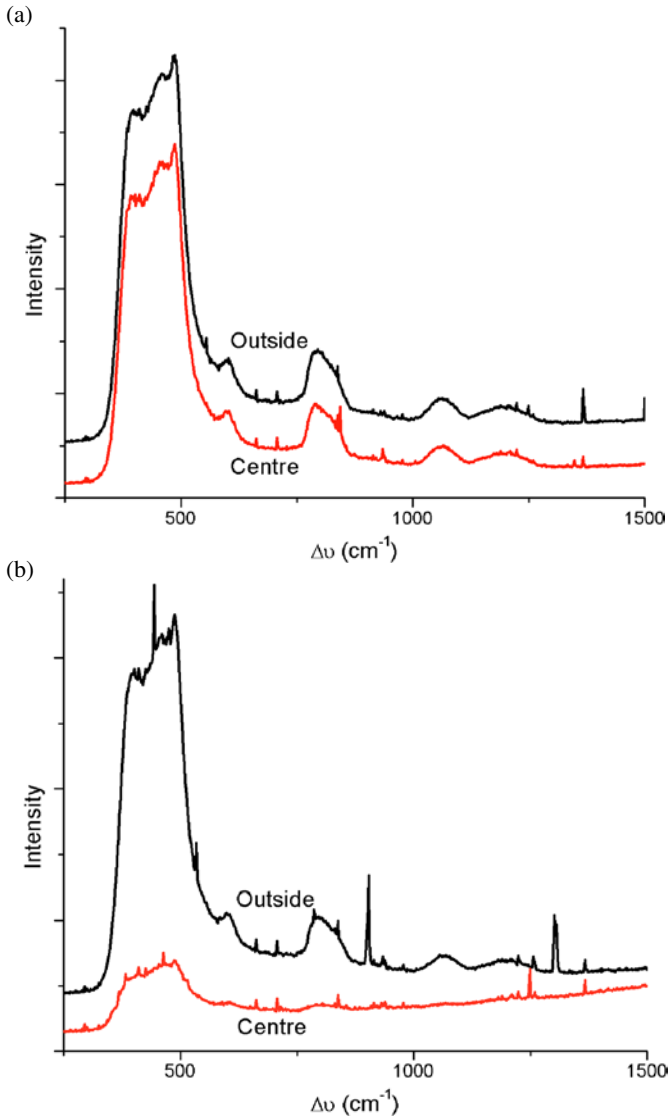

Figure 4. Raman spectra measured from regions inside and outside lines written in fused silica with a 6 cm focal length lens and (a) 9 μJ and (b) 25 μJ fs laser pulse energy. The sharp spikes in the spectrum are due to random noise resulting from the long acquisition times. The rising tail in the 'centre' spectrum of (b) is due to fluorescence.

determining the defect profile, so it is possible that the actual profile has much sharper edges similar to those reported in [22].

The Raman results do not lend themselves to a simple explanation. If we use the 605 cm^{-1}/800 cm^{-1} peak intensity ratio as a measure of the local density then, first of all, the density seems to be only slightly higher than that of the unmodified glass and, secondly, there seems to be no variation in density across the modified region. But that still leaves the decrease in overall Raman intensity to be explained. One could argue that the central region contains a rarefied amorphous material with a very high concentration of broken bonds. Since

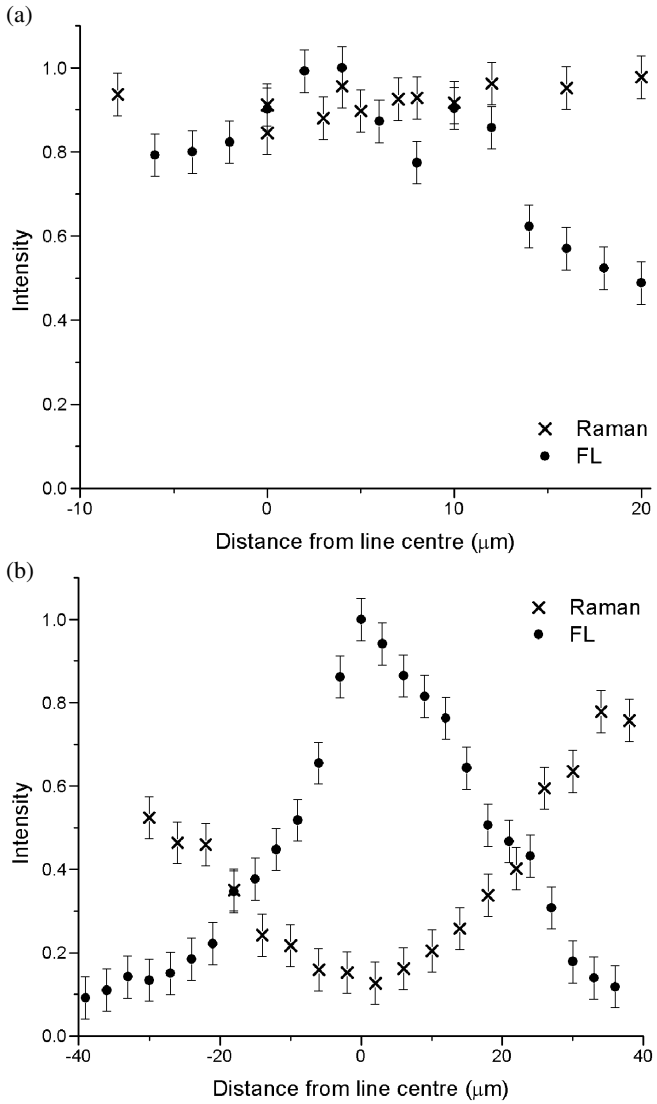

Figure 5. Fluorescence (♦) and Raman (×) intensity as a function of distance from the line centre for lines written in fused silica with a 6 cm focal length lens and (a) 9 μJ and (b) 25 μJ fs laser pulse energy.

the overall Raman intensity can be thought of as resulting from the product of the number of 'bonds' and the 'bond polarizability', such a rarefied material could account for a decrease in Raman intensity together with an increase in fluorescence intensity. However, the change in Raman signal could also be the result of the fact that a substantial fraction of the Raman scattered light is lost due to elastic scattering/absorption, as it travels through the sample from the plane of observation (focal plane) to the detector. This loss will be higher in the modified region since it is optically less homogeneous especially for higher fs laser fluences. The total loss will scale with the laser fluence, and will increase as the focal plane of observation moves deeper into the sample. Further experiments in which the focal plane (plane of observation)

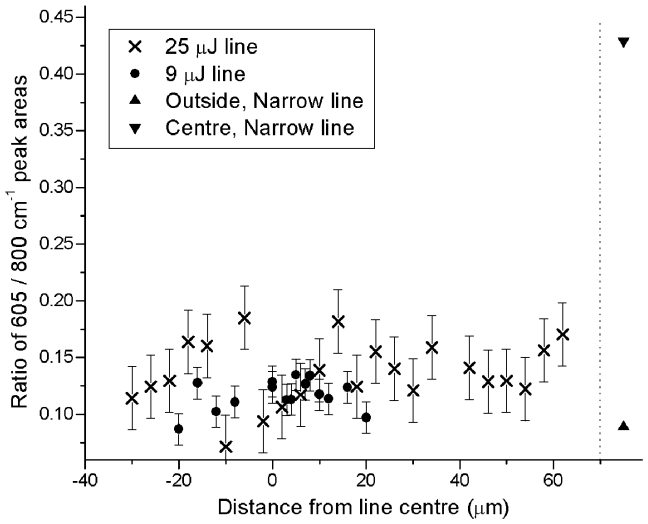

Figure 6. The intensity ratio of the 605 and 800 cm^{-1} Raman peaks as a function of distance from the line centre for lines written in fused silica with a 6 cm focal length lens and 9 μJ (●) and 25 μJ (×) fs laser pulse energy. For comparison the 605 cm^{-1}/800 cm^{-1} ratio in the centre of (▼) and outside (▲) a narrow line written with a 50×, 0.55 NA objective and 4 μJ fs laser pulse energy is also shown.

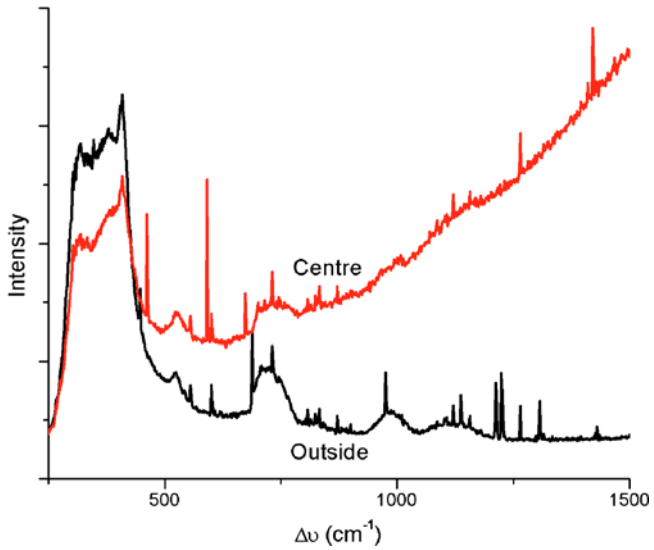

Figure 7. Raman spectra measured from regions inside and outside a line written in fused silica with a 50×, 0.55 NA objective and 4 μJ fs laser pulse energy. The sharp spikes in the spectrum are due to random noise resulting from the long acquisition times. The rising tail in the 'centre' spectrum is due to fluorescence.

was moved deeper into the sample indicate that this decrease is indeed, at least partially, due to scattering/absorption. As expected, these effects were enhanced by the use of greater pulse energies. Of course the fluorescence signal would experience a similar loss, and taking this into account means that the fluorescence intensity generated from the modified region is even higher than what is detected.

In conclusion, our results do not show an unambiguous indication of density variations across the modified lines. A recent study by Taylor *et al* [22], in which an ultrahigh-resolution (20 nm) spatial profiling technique—based on a combination of selective chemical etching and AFM—was used to probe index/structural variations across a fs laser-modified line of 2 μm diameter, also did not find any low-density region. It is possible that the focusing conditions used in our writing experiments could have led to self-focusing [4] which could have led to a less effective deposition of the laser energy in the focal volume, but for the writing conditions used in [22] self-focusing does not play a role. Clearly, further in-depth experiments are necessary to fully characterize and understand the microstructure inside laser-written lines in fused silica.

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