Inscription and characterization of micro-structures in silicate, FOTURAN^{TM} and tellurite glasses by femtosecond laser direct writing

K.C. Vishnubhatla,[1] S. Venugopal Rao [2,*], R. Sai Santosh Kumar,[1] K. Shiva Prasad[3], P.S.R. Prasad,[3] and D. Narayana Rao[1,#]

[1] School of Physics, University of Hyderabad, Hyderabad 500046, India
[2] Advanced Centre of Research in High Energy Materials (ACRHEM), School of Physics
University of Hyderabad, Hyderabad 500046, India
[3] National Geophysical Research Institute, Hyderabad 500007, India

ABSTRACT

We present some of our results on the femtosecond laser direct writing and characterization of micro-structures in silicate, Foturan^{TM}, and tellurite glasses. Structures with different sizes were fabricated with varying input energy and spatially modified pulse using a slit. Various characterization techniques including fluorescence spectroscopy, micro-Raman spectroscopy, and laser confocal microscopy were employed to analyze the structural and physical modifications at focal volume resulting in the change of refractive index (RI). The RI change due to material modification was estimated using diffraction from a continuous wave laser beam and is presented in this work. The results obtained are analyzed vis-à-vis the recent work in similar glasses and the applications of such structures in the fields of photonics.

Keywords: Femtosecond direct writing, Multiphoton absorption, Foturan, Micro-structures

1. INTRODUCTION

The ability to pattern (process, deposit, dispense, or remove) materials in three dimensions and pre-determined manner is attractive for several emerging technologies like photonics and microfluidics.[1,2] Femtosecond direct writing is capable of creating three dimensional micro-structures deep inside bulk of a dielectric or polymeric material.[3-13] Direct writing using ultrashort pulses offers exciting prospects for miniaturization and integration of highly functional photonic and microfluidic devices directly inside transparent dielectrics and polymers alike.[14-16] In contrast to standard methods such as physical-vapor deposition or ion exchange, direct write approach is not constrained to the surface and yields truly three-dimensional structures. Femtosecond pulses when focused possess the unique ability to precisely deposit energy inside the material. The ultrafast interaction does not require specially prepared or photosensitive materials rendering it a superior technique. Several photonic and microfluidic structures/devices have been demonstrated recently ratifying the great potential of this technique. Some of the diverse structures/devices produced using this method are (a) Waveguides in laser crystals such as Ti:Sapphire, Nd:YAG ceramics[17-19] (b) Variety of microfluidic structures in Foturan^{TM} leading to lab-on-a-chip devices[12] (c) Polymeric photonic structures in PMMA (Poly Methylmethacrylate)[20,21] (d) Waveguides in periodically poled lithium niobate (PPLN)[22-24] (e) Waveguide lasers in the telecom band[25,26] (f) Micro and nano channels in variety of materials[27,28] (g) Photonic crystal structures in glasses and polymers etc.[13,16] Among some of the interesting applications include the utilization of femtosecond direct writing in joining/welding two similar and dissimilar glasses.[29] Femtosecond direct writing also finds applications in polymers with good two photon absorption coefficients. The field of two-photon polymerization has expanded over the last few years and is now mature to fabricate photonic and microfluidic devices.[15,16] Here, we present some of our results on the direct writing and characterization of micro-structures in silicate, Foturan^{TM}, and tellurite glasses. Structures with different sizes and shapes were fabricated with varying input energy and spatially modified input pulses using a physical slit. Various characterization techniques including fluorescence spectroscopy, micro-Raman spectroscopy, and confocal microscopy were employed to analyze the structural and physical modifications. The RI change resulting from high peak intensities of the focused femtosecond (fsec) pulses was estimated using diffraction from a continuous wave laser beam and is presented. Applications of the structures created in these glasses are also discussed.

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e-mail: *svrsp@uohyd.ernet.in, # dnrsp@uohyd.ernet.in, Fax: +91-40-23011230

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2. EXPERIMENTAL

2.1 Sample preparation:

All the samples were typically cut to a dimension of 1cm X 2 cm for ease of use and all the 6 faces were optically polished. Samples were first cleaned using acetone and then with methanol to ensure that the surface is devoid of any stains and dust. The cleaned samples were placed on computer controlled XYZ stages with nano-precision for better control over the structures to be written in them. Figure 1 shows the schematic of the experimental setup. The quality of the structures fabricated depended critically on the quality of the focused spot and the movement of the sample placed on XYZ stage. Any aberration in the optics or stage movement affected the shape and size of the structures drastically. Typically 100 fsec pulses from an amplifier were employed for direct writing at of 800 nm with 1 KHz repetition rate. Neutral density filters were used to attenuate the beams. The beam was steered such that it focuses downwards on to the sample after the microscope objective (typically 40X, 0.65 NA). Typical writing speeds of 50-100 μm/sec were used.

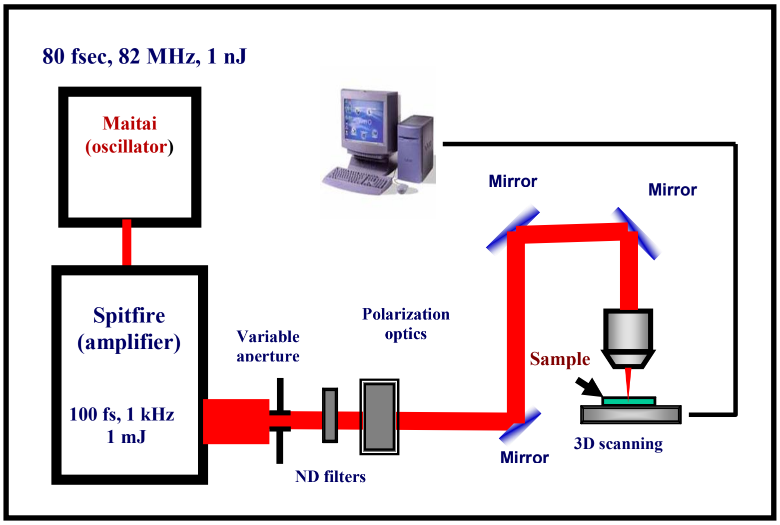

Figure 1 Schematic of the experimental set up used for femtosecond direct writing.

2.2 Inscription of grating:

The procedure followed for inscribing and characterizing the gratings is as follows. Initially simple straight line structures were inscribed into samples. Each line corresponded to a specific set of parameters (like the sample translation speed, intensity of the fsec pulses, and size of the aperture before the microscope objective). Later these structures were imaged using Leica scanning confocal Microscope. Images were obtained both in transmission mode and reflection mode. The imaging essentially takes advantage of deferential transmission and reflection properties of the samples in the regions exposed to the femtosecond laser and the un-exposed regions. In the transmission mode the width of the structures was determined. In the reflection mode several snapshots of the structures were taken along the depth at definite intervals (typically the step size along the z is chosen to be ~1 μm). Each snapshot corresponded to a particular depth and all these snapshots were collated to obtain a 3-D (cross-sectional, depth profile) view of the structures written.

3. RESULTS AND DISCUSSION

3.1 Fused Silica:

The sample was translated perpendicular to the written line by a definite distance and then another line was inscribed. In this manner a set of about 100 parallel lines were inscribed creating a periodic alternating regions in the sample exposed and un-exposed to fsec laser irradiation. These periodic regions of modified and unmodified RI act as a grating. These grating structures inscribed in glasses were utilized to estimate the change in refractive index due to fsec laser modification from the grating efficiency measurements. Figure 2 shows the gratings inscribed in (a) fused silica and (b) GE124 glass which is a variant of silicate glass (Fused Quartz/Silica). The main differences are that fused quartz has a much lower OH content and fused silica transmits better in the UV. Both are highly pure, have high chemical resistance, good thermal shock resistance, and low thermal expansion coefficient. Inset of the figure shows the images of optical diffraction. A He-Ne laser (633 nm) beam was incident perpendicular to the plane of the gratings and, the internal diffraction images were recorded on a screen placed 10 cm away from the sample. The intensities of the different laser spots corresponding to the different orders of diffraction which were measured using Ophir make power meter. The grating diffraction efficiency was calculated to be 20.3% for the first order. The change in the refractive index (Δn) is estimated to be of the order of 10^{-3} using the equation 1.

$$\Delta \mathbf{n} = \lambda\ \cos\theta\ \tanh^{-1}(\sqrt{\eta})\ /\ (\pi\ \mathbf{d}) \tag{1}$$

Where η is the diffraction efficiency fraction of first order to the zeroth order, λ is 632nm, θ = 90 degrees, d is the depth or the grating thickness. The Δn values obtained for the gratings are summarized in table 1. Similar procedure is adapted for measurements of diffraction efficiency of gratings in other glasses

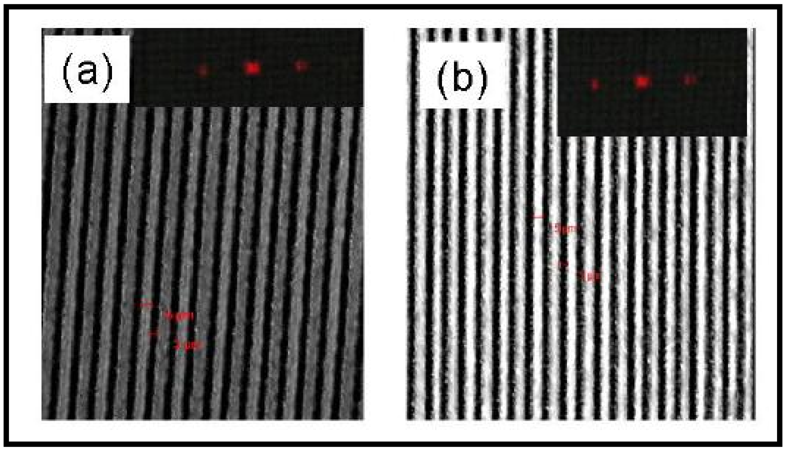

Figure 2 Gratings written in (a) Fused silica glass and (b) GE124 glass. Inset shows the optical diffraction pictures

The 2 D micro gratings in figure 3 (a), (b) were realized three sets of parallel lines inscribed making an angle of 60 degrees with respect to each other. This is to demonstrate the ability of this process to create any structure, potentially leading to the fabrication of 2D-photonics crystals by LDW.

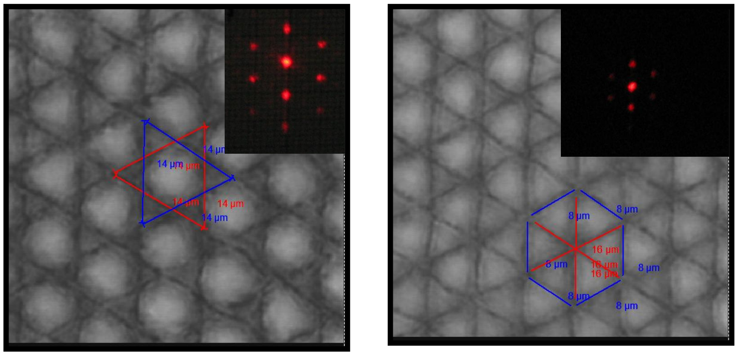

Figure 3 Confocal images of the two dimensional gratings written in (a) Fused silica glass. Inset shows the optical diffraction pictures

3.2 Spectroscopic characterisation of the micro-structures:

Several groups have been working recently on direct writing in fused silica with fsec pulses for making simple passive structures, channels, etc.[30-64] However, the mechanism for RI change caused by the fsec pulses is still being debated. It is essential to understand the physical mechanism responsible for RI change in the inscribed structures for optimization of the structures making them eligible for device applications. To analyze the interaction of fsec pulses with fused silica glass network we performed micro-Raman measurements in the fsec laser-irradiated and non-irradiated regions of the sample. The samples were excited with 514 nm and figure 4(a) shows the micro-Raman spectra obtained in two regions of the fused silica sample studied. Black curve represents the spectrum obtained from the region unexposed to fsec while the red (dashed) curve for the region irradiated with fsec laser. The fused silica structural network typically has predominantly large 5- and 6-fold ring structures. The increase in the intensity of the peak at 600 cm^{-1} is ascribed to the change in ring statistics where six-fold rings transform to threefold and fourfold rings after laser irradiation. An increase in the number of smaller 3- and 4-fold ring structures leads to a decrease in the overall bond angle and a densification of the glass. Earlier reports[33,34] also suggest that the possible mechanism of wave guiding in fused silica glass to be breakage of bonds in the network leading to densification and hence increase in refractive index in that region.

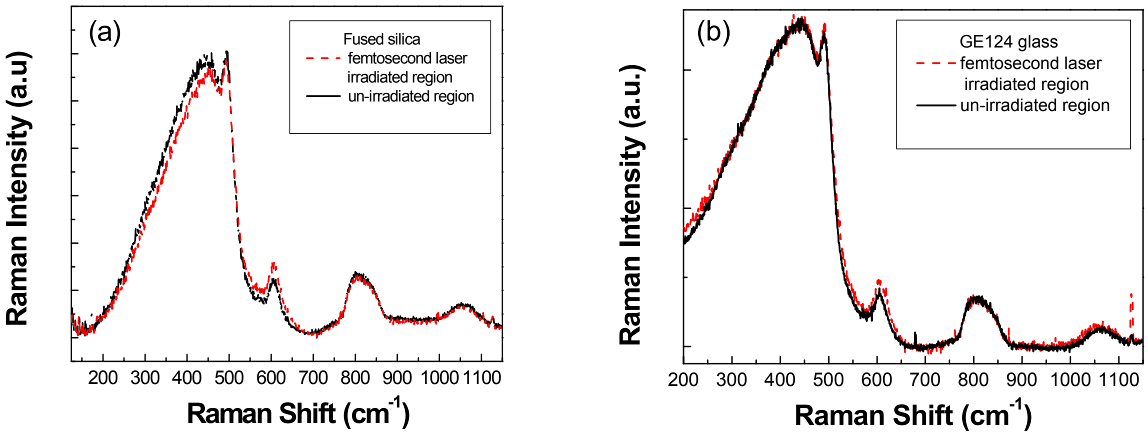

Figure 4 micro-Raman spectra obtained from irradiated and non-irradiated regions in (a) Fused silica (b) GE124

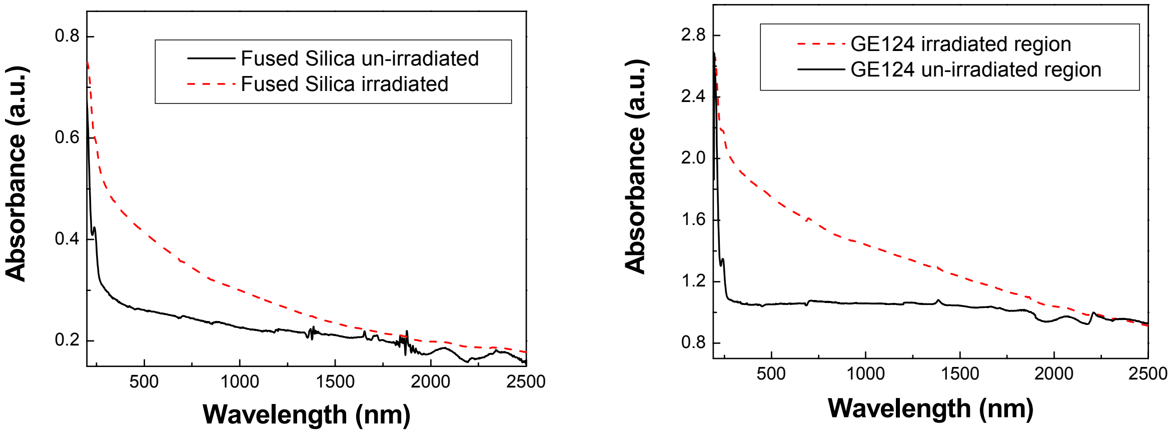

Figure 5 Absorption spectra of the pristine fused silica (solid) and that of the region where waveguides were written (Dashed). (a) Fused Silica (b) GE124 glass.

The spectrum obtained in GE124 glass, shown in figure 4(b) was similar to that of the spectrum obtained in fused silica. There are several reports of waveguides, gratings, and micro-channels fabrication in fused silica. The RI change achieved varied from 10^{-3} to 10^{-4} depending on the writing conditions. For further investigation we looked at the absorption spectra of the modified and pristine regions of the fused silica sample. Figure 5(a) shows the spectra for fused silica glass. Clearly there is a change in the absorption (Dashed represents the spectrum from modified region whereas the solid line represents the spectrum from pristine region. The spectra of the FS and GE124 are similar and the increase in absorbance from the written region could possibly be attributed to the absorption resulting from the defects created during the process of LDW. Another probable mechanism could be the scattering losses resulting from the gratings inscribed. Further studies are in progress for a better understanding of this mechanism.

3.3 Zinc-Tellurite glass:

Tellurite glasses have high refractive index compared to silicate glasses. This induces the increase of local field around the rare earth ion causing the enhancement of the radiative transitions and a wider splitting of Stark sublevels. Consequently greater efficiency and broadening of the emission shape is observed. These properties prove to be important for Wavelength Division Multiplexing applications. The extension of LDW method to fabricate waveguides was less successful till recently. Tokuda et al.[65] reported longitudinal writing of relatively short waveguides and positive refractive index change in niobium tellurite glasses. In contrast reports also indicate negative refractive index change making a waveguide impossible.[66] Nandi et al.[67] has recently demonstrated the wave guiding in Er doped tellurite glasses co-doped with phosphate. The nonlinear coefficients of tellurite based glasses being very high, the incident laser intensity required would be less as compared to silicate glasses which is evident from the table 4.1. Only a third of the average energy was used (compared to fused silica) to inscribe the structures. Micron sized gratings were inscribed in tellurite glass and the optical diffraction efficiencies were measured. The change in refractive index due to the laser irradiation was calculated to be 2.025×10^{-3} (see Table 1). The confocal-microscope image of the grating and its internal diffraction pattern is depicted in the figure 6. We could control the grating period along with the grating spacing and achieved periods in the 4-10 μm range. Realizing passive structures such as waveguides, gratings in these glasses will enhance their device capabilities, especially for telecommunication applications. By proper co-doping we can accomplish active devices also.

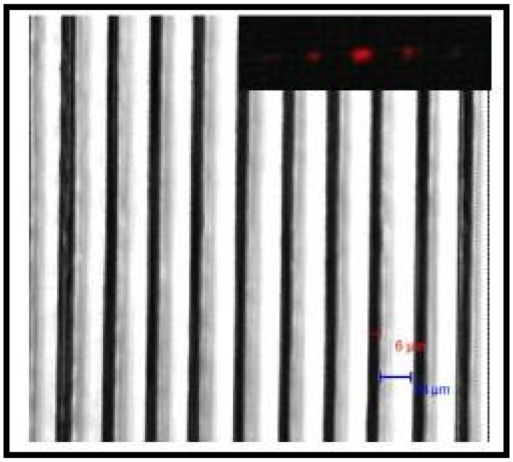

Figure 6 Confocal image of the **g**rating written in tellurite glass. Inset shows the optical diffraction picture.

3.4 Foturan glass:

Foturan, a photosensitive glass is one of the most successfully commercialized glasses manufactured by Schott Glass Corporation. It comprises lithium aluminosilicate glass doped with trace amounts of silver and cerium. The cerium (Ce^{3+}) ion plays an important role as photosensitizer, which releases an electron to become Ce^{4+} with exposure to UV light. Some silver ions are reduced by the free electrons and silver atoms are created. However, in the case of fsec laser irradiation, free electrons are generated by inter-band excitation due to multi-photon absorption for silver atom precipitation. Therefore, Ce^{3+} doping is not necessary for fsec laser micromachining applications. In the subsequent heat treatment the silver atoms diffuse and agglomerate to form nanoclusters at about 500^0 C followed by the crystalline phase of lithium metasilicate which then grows in the amorphous glass matrix in the vicinity of the silver nanoclusters, acting as nucleus, at about 600^0 C. Since the crystalline phase of lithium metasilicate has higher solubility in a dilute solution of HF acid than the glass matrix it can be easily etched away leaving behind empty channels/voids. Midorikawa et al. has reported results from their pioneering work of fsec modification in Foturan^{TM} for applications in lab-on-a-chip and microfluidics.[68-75] Different structures fabricated in Foturan glass using ultrashort pulses include waveguides,[76,77] micro-mechanical and micro-optical components, microfluidic dye lasers, and microchannels, all integrated on a single chip leading to lab-on-a-chip device applications.[68-75]

Micro-gratings were inscribed inside Foturan^{TM} glass with different grating periods. Figure 7(a) shows the confocal image of a typical grating in Foturan^{TM}. The change in refractive index was estimated to be 2.24×10^{-3} from the diffraction efficiency measurements. The absorption spectrum collected from the modified region illustrated an apparent increase in absorbance. This can be attributed to formation of color centres associated with Ag^{+}. Raman spectrum from the laser-irradiated region could not be obtained due to strong fluorescence covering the Raman bands. Confocal photoluminescence (PL) was obtained by exciting the sample with 457 nm, 488 nm, 514 nm spectral laser lines. The confocal microscope was used in the XY-lambda mode. In this mode the microscope collected the photoluminescence from the region of interest in the sample over the range specified in intervals typically of 3 nm width.

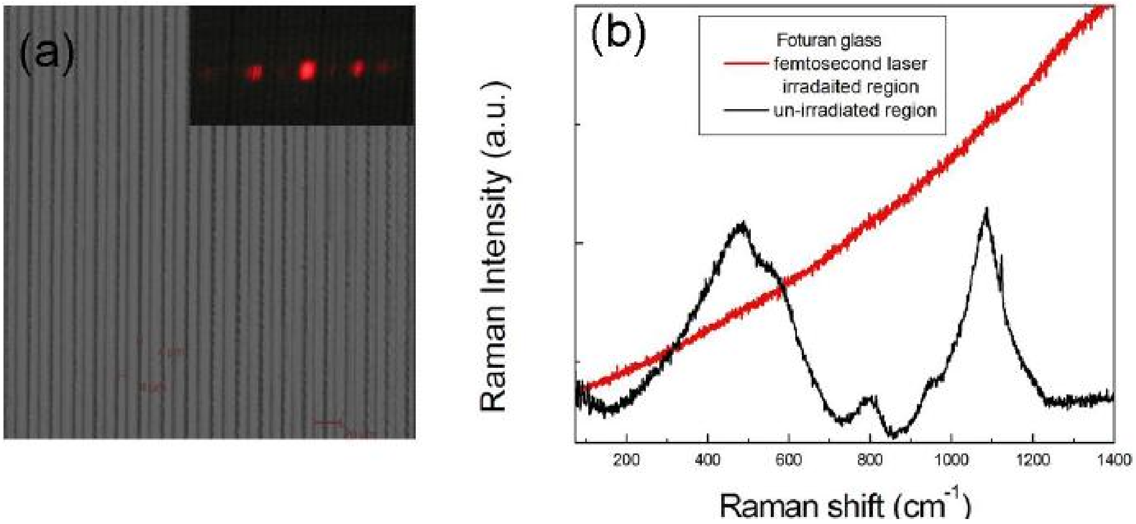

Figure 7(a) Confocal image of the grating in Foturan glass and the inset shows the diffraction image. (b) micro-Raman spectrum of the irradiated region in Foturan^{TM}.

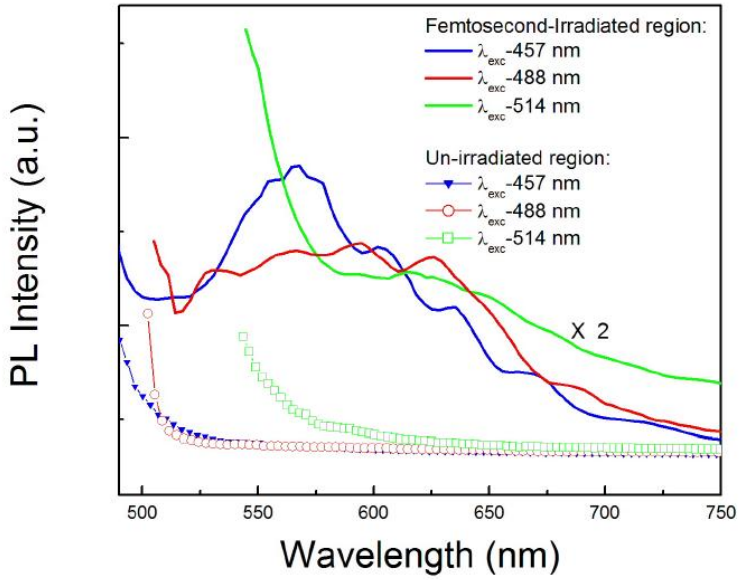

Figure 8 Photoluminescence spectra of the fsec laser irradiated region in Foturan^{TM}

The region of interest in the sample was excited with laser light and the photoluminescence was collected for a specified time interval from the entire region of interest. Photoluminescence in this band of wavelength was stored as intensity pattern. The collection window then moved to the next consecutive band of wavelength and the PL was recorded. This process was repeated until the entire specified range of wavelength is scanned by changing the collection window. Once the entire range was scanned the intensity patterns corresponding to the various wavelength intervals were integrated to obtain a plot of intensity versus wavelength. Interestingly only the region irradiated with fsec laser showed clear photoluminescence band. The centre of the band shifted with the excitation source wavelength (see figure 8). Though this kind of photoluminescence was observed in Ag doped Phosphate glasses,[78] to our knowledge this is the first time being observed in Foturan glass. We expect the presence of color centers in the light modified regions contributing to the observed PL. Interestingly, PL was observed from the region modified by the laser irradiation (relatively higher refractive index) only. Since this glass is being used proficiently for micro-fluidic applications the observation of PL becomes important from the glass since this will find applications in microfluidics and fluorescence sensors.

Sample	Incident Energy	Dimension of structure	Grating period	Efficiency (%)	Δn (× 10^{-3})
Fused Silica	60 μJ	4 μm	4 μm	0.20	2.420
GE124	65 μJ	5 μm	5 μm	0.21	2.490
Tellurite	20 μJ	6 μm	10 μm	0.14	2.025
Foturan	65 μJ	4 μm	4 μm	0.18	2.240

Table 1 Summary of the dimensions of the structures achieved in various samples along with the efficiencies of the diffraction and the corresponding RI change measured.

Table 1 summarizes the results presented in this paper. Following the success in fabricating grating structures we would proceed to fabricate waveguides and micro-channels in these glasses thereby leading to simple devices. The ability to fabricate such structures in various glasses has implications in various fields of telecommunications and biotechnology. Integrating simple passive structures such as waveguides, gratings, couplers, splitters, etc. along with active devices such as laser sources, detectors will lead to photonic integrated circuits while integration of optical components and microfluidic components like channels, reservoirs, etc. will lead to optofluidic lab-on-a-chip devices capable of on-site diagnosis. The quality of structures fabricated in dielectrics depends on several factors like wavelength and repetition rate of the femtosecond source, focal conditions, pulse duration, pulse energy, and writing speeds. The mechanism by which the refractive index is modified with femtosecond pulses depends critically on the glass composition and the writing conditions.[79-88] The commonly accepted explanation is of energy deposition into the matrix via non-linear or multi-photon absorption leading to restructuring of the material. It has also been proposed that densification results when the molten material re-solidifies. Some of the proposed mechanisms responsible for refractive index changes resulting from femtosecond pulse interaction with glasses include (a) Densification (compaction) through bond breaking (b) Color center formation which alters refractive index (c) Thermal melting followed by re-solidification leading to higher index core required for wave guiding. It was also suggested that a combination of these effects could be present, depending on exposure conditions of the ultrafast laser. Three important regimes have been identified by Hnatovsky et al.[23,32] in their recent work: (a) Type I damage: Homogenous modification associated with smooth RI change (b) sub-wavelength nano-gratings produced with linearly polarized laser and disordered nanostructures with circularly polarized laser and (c) Disruptive modification (e.g. voids, micro-explosions). The mechanism of ultrashort-pulse modification of transparent materials can be divided into several steps: (1) Production of initial seed electrons through non-linear photo-ionization of free electrons or excitation of impurity defects, (2) avalanche photo-ionization, (3) plasma formation, and (4) energy transfer from the plasma to the lattice.

4. CONCLUSIONS

We have successfully fabricated micro gratings in silicate, Foturan^{TM}, and tellurite glasses using femtosecond direct writing. Refractive index change in these structures was estimated using optical diffraction technique and was found to be in the order of 10^{-3} sufficient for wave guiding applications. Several characterization techniques were used for insight into the fsec interaction with the glass matrix. The ability to create such structures, both passive and active, has strong implications in the field of micro-photonic and microfluidic devices.

5. ACKNLOWEDGMENTS

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