Investigation and control of ultrafast laser-induced isotropic and anisotropic nanoscale-modulated index patterns in bulk fused silica

R. Stoian,1,∗ K. Mishchik,1 G. Cheng,2 C. Mauclair,1 C. D’Amico,1 J. P. Colombier,1 and M. Zamfirescu3

1Laboratoire Hubert Curien, UMR 5516 CNRS, Université de Lyon, Université Jean Monnet, 42000 Saint Etienne, France
2State Key Laboratory of Transient Optics and Photonics, Xi’an Institute of Optics and Precision Mechanics, CAS, 710119 Xi’an, Shaanxi, China
3National Institute for Laser, Plasma and Radiation Physics, 077125 Magurele, Bucharest, Romania
∗razvan.stoian@univ-st-etienne.fr

Abstract: Ultrafast laser-induced refractive index changes in a-SiO2 consist, depending on the irradiation conditions, of either positive variations, voids, or regular nanoscale patterns, each of these underlying specific structural transformations. These allow for obtaining a large palette of optical functions ranging from low loss guiding to anisotropic scattering. While briefly reviewing the excitation mechanisms, we spectroscopically interrogate local electronic and structural transformations of the glass in the isotropic index zones and in the regular self-organized nanostructures, indicating bond breaking and matrix oxygen deficiency. A spatial defect segregation marks the material transformation in the different photoinscription regimes. We equally propose a method of real time control of nanogratings formation under the action of ultrashort laser pulse with variable envelopes. Application as polarizing optical devices is discussed.

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1.

Introduction

Local refractive index changes are the building blocks of laser-induced three-dimensional (3D) optical functions in transparent materials, e.g. fused silica (a-SiO2) [1–9] and the laser-assisted material transformation has imposed itself as a unique method of volume fabrication. Index changes are typically obtained by focusing and scanning ultrashort laser pulses in the bulk of the material. The emergence of a carrier plasma at the focal point allows transferring the laser energy to the material on micron and sub-micron scales. Subsequently, a change of the dielectric function occurs due to either electronic or structural material transformations, carrying an optical signature. We discuss below the role of nonlinear interaction, the subsequent material response in optical functionalization of the dielectric fused silica matrix, and the consequences for optical photoinscription and system fabrication. These justify a set of morphology and structural investigations serving as a basis for further control options with engineered beams.

1.1. Linear and nonlinear effects

The efficiency of the energy conversion depends strongly on the focusing conditions, as nonlinear absorption and particularly nonlinear propagation of the laser pulses play a fundamental role. The establishment of an embedded optical object puts forward two points of interest; the optical distribution of energy and the material reaction to the sudden energy input. The moderate focusing conditions (numerical apertures NA=0.3–0.6) usually employed in laser photoinscription are typically at the frontier between a filamentary propagation and material breakdown before the onset of (power-dependent) nonlinearities. The mechanisms of absorption involve in most cases multiphoton processes and the determination of local intensities is of utmost importance. Upon propagation of a short pulse the local intensities at the excitation region can be strongly affected, impacting the quantitative evaluation of the excitation efficiency. An example of the occurrence and the influence of the nonlinear effects, mainly Kerr self-focusing and defocusing on carrier plasmas [10–13], upon focusing of ultrashort laser pulses (120 fs) is illustrated for a beam waist of $\omega = 0.9 \, \mu m$ in Figs. 1(a)–1(d) within the optical nonlinear Schrödinger equation (NLSE) formalism. Calculations indicate a strong difference of the locally achieved fluences (Figs. 1(a) and 1(b)) and intensities (Figs. 1(c) and 1(d)) between linear and nonlinear cases for similar input conditions. The balance between the optical Kerr effect
inducing additional convergence and carrier defocusing determines a spatially and temporally modulated energy deposition, with an asymmetric energy deposition maximizing before the geometrical focus [12]. An example of how different time slices of the input pulse are spatially distributed inside the material is given in Fig. 1(e), for a pulse energy above the self-focusing threshold (200 nJ for 2 MW critical power), showing how the input exposure shifts from the focus and agglomerates towards the laser source during irradiation [12]. This non-uniform energy exposure creates the conditions for site-specific electronic and thermo-mechanical scenarios of
material transformation [14]. These conditions can be relaxed by using tight focusing geometries or longer pulse durations, when the particular material response (rarefaction, densification) takes the lead in establishing the final refractive index modification.

1.2. Material effects

The a-SiO₂ is a model material for investigating the effects of ultrafast laser irradiation. It has a low density among the class of 4-coordinated silica polymorphs (from fused silica, quartz to coesite). The relaxation of the laser generated carriers with typical energies around 10-15 eV leads to a succession of events that may compete or synergetically reinforce each other [14–23]. The relatively strong electron-phonon coupling in fused silica leads to polarization effects in the dielectric matrix and carrier trapping, driving local atomic deformations and displacements, bond breaking, and electronic localization in form of excitons and defects. These determine changes in both the energetic structure and the dielectric function. At the same time a parallel and competing process of matrix heating and vibrational enhancement takes place, affecting the rigidity of the matrix and depositing energy as heat. As the temperature increases, the structure reassembly in new arrangements, culminating with viscosity decrease, pressure release and stress generation, and eventually phase transitions, with the series of events extending from ns to μs. A graphical representation of the succession of processes with their characteristic times is given in Figs. 2(a)–2(c).

Relying on these material transformation stages, ultrashort pulses could therefore induce positive isotropic smooth refractive index changes (usually denoted as type I), local void-like
Fig. 3. Type I and II laser-generated traces and the underlying isotropic index change or nanogratings in a-SiO₂ for various irradiation conditions at 100 kHz repetition rate and NA=0.42 focusing [27]. (a) Phase contrast microscopy images of type I modification traces in static (single and multishot) and longitudinally scanned conditions; dark and white are positive and negative index changes respectively. (b,c) Phase contrast microscopy images of type II modification traces in static and longitudinally scanned conditions with nonguiding (NG) and guiding (WG) properties. SEM cross-section of the traces showing the nanoscale arrangement are given together with corresponding guided modes at 800 nm. We note isotropic mode transport for type I traces and polarization type II guiding for electric field parallel to the nanoplanes. (d,e) Bulk nanograting patterns induced by radial and azimuthal polarization. (f,g) Indication of the pulse duration effects in localizing higher amounts of excitation with consequences in void dimensions [27]; single shot structures. (h) Void movement and merging with increasing number of pulses (N=1-50 at 1 Hz) suggesting the development of low viscosity phases (Media 1).
and type II trace morphologies. The transition from type I to type II as a function of energy and number of pulses (Figs. 3(a)–3(c)) in static and scanned regimes, the orientational effect of nanogratings in response to pulse polarization (Figs. 3(d) and 3(e)), the role of voids and the pulse duration influence in determining void dimensions (Figs. 3(f) and 3(g)) are equally depicted, with an illustrative display of the development, movement, and merging of voids in Fig. 3(h)(Media 1). The figure points out clearly that the excitation dose and exposure time characteristics have a strong influence on the topology of the laser-induced phase object. A type I morphology appears facilitated by low doses and ultrashort pulses, while type II aspect is reinforced by high doses and slightly longer pulse durations due to a stronger energy confinement assisted by weaker plasma defocusing as compared to the ultrashort case. This facilitates dimensional increase of voids, voids merging in low viscosity phases and the seed of hydrodynamic nanoscale rearrangement of matter [27]. The origin of the different photoinscription regimes is subject of ongoing debate and various hypotheses were put forward, from plasma wave interactions to localized deformable nanoplasma zones, or thermodynamic behavior of atypical glasses [24, 25, 28]. In all these models, the level of excitation achievable via the pulse form and the subsequent material modification phases play a fundamental role.

In this context a study of morphological and structural material properties upon laser excitation in addition to the laser-generated optical functions is particularly useful. We review here topological and space-resolved spectroscopy results revealing particular electronic and structural transformation of the glassy matter in isotropic index domains and in the self-organized subwavelength structures, indicating bond breaking and, respectively, an abundance in oxygen deficiency. Electronic densification mechanisms are proposed for soft uniform index increase and hydrodynamic processes for nanogratings zones. As the spontaneous arrangement is intermediated by electronic excitation, we equally propose a method of real time control of nanogratings formation under the action of laser pulse with programmable variable envelopes, leading to a period tunability. Relying on the advantage of intrinsic anisotropies, the application potential in terms of polarization sensitive optical devices is discussed.

2. Experimental setup

Ultrashort 800 nm light pulses from two laser systems were employed to irradiate bulk a-SiO$_2$ glass samples; a regeneratively amplified Ti:sapphire ultrafast laser system delivering 300 mW of power at a repetition rate of 100 kHz and a nominal output pulse duration of 130 fs, and a regeneratively amplified 1 kHz Ti:sapphire laser system providing 120 fs laser pulses at pulse energies of up to 1 mJ. Repetition rates and exposure doses were controlled using externally-driven Pockels cells and electromechanical shutters. Polished a-SiO$_2$ parallelepipedic samples were employed, mounted on a XYZ motion stage that allows translation parallel or perpendicular to the laser propagation axis. The beam was focused inside the target by various focusing optics including long working distance high, moderate, and low numerical aperture objectives. Static and longitudinal writing configurations with translation parallel to the laser propagation axis and in the direction of the laser source were used. An Olympus BX 41 positive optical phase-contrast microscope was employed to image the interaction region in a side-view geometry. The relative positive index changes are appearing dark on a gray background, while white zones indicate negative index variations or scattering centers. The phase contrast microscopy (PCM) and the optical transmission microscopy (OTM) were accompanied by white light transillumination imaging (WL), scanning electron microscopy (SEM), photoluminescence (PL) and Raman confocal micro-spectrometry. Additionally, the guiding properties were verified upon injection with IR and visible light.

The PL and Raman spectra of the photoinscribed traces were recorded with a confocal photoluminescence and Raman microspectrometer in a backscattering configuration (Horiba Jobin...
Yvon Aramis) with micrometric spatial resolution. Three laser sources were used for excitation, offering four excitation wavelengths: HeNe laser light at 633 nm (1.96 eV), Argon ion (Ar$^+$) laser radiation at 488 nm (2.54 eV), and coherent photons from a HeCd laser at 442 (2.81 eV) and 325 nm (3.82 eV). These wavelengths usually cover the excitation bands of non-bridging oxygen hole centers (NBOHC) and oxygen deficiency centers (ODC) as markers of bond breaking.

3. Discussion

3.1. Electronic and structural modifications in the α-SiO$_2$ matrix

We have identified so far the optical and topological aspects of the different photoinscription type I and type II results, with their positive index uniform increase, void appearance, and nanoscale index modulation. After determining the respective change of morphologies, a relevant question refers to the structural modifications characterizing the glass network in type I and type II regimes. During photoinscription coherent radiation is emitted as harmonics (see Fig. 2(a)), indicating anisotropic electronic movement [30]. In addition, incoherent radiation marks post-irradiation electronic and structural transformations that can be evidenced by using defect resonant and nonresonant excitation. The presence of electronic defects and laser-induced changes in microscopic structures were discussed in many occasions due to their potential in revealing essential glass transformation paths [17, 18, 20, 31] either via thermal trajectories (fictive temperature) or electronically-driven local densification. These are equally potential drivers for laser-induced refractive index changes or local changes of material properties where accepted scenarios indicate bond-breaking and structural modification (an increase in the number of three and four member rings in the silica matrix) or mechanical compaction and rarefaction effects. With respect to refractive index changes, the relevant question is in which proportion the electronic and thermal paths contribute and what are the corresponding conditions of exposure.

The nonlinear energy distribution resulting in space-modulated index changes puts also forward the necessity of a space-resolved study that can correlate material modifications in type I and type II ranges with local accumulated doses. Here PL studies performed in a space-resolved manner indicate the presence of several types of defects in the irradiated regions [30, 32] with the results given in Figs. 4(a) and 4(b). Two main PL issues can be underlined both spatially (Fig. 4(a)) and spectrally (Fig. 4(b)). For type I traces HeNe 633 nm resonant excitation of NBOHC centers probed by 1.9 eV (650 nm) PL (see NBOHC PL spectra in Fig. 4(b)) reveals a preferential generation of NBOHC in the positive index regions via a probable precursor self-trapping mechanism (Fig. 4(a) left). Type II modifications and especially the nanopatterned regions show a different type of defect spatial distribution (Fig. 4(a) right). Ar$^+$ excitation at 488 nm, though relaxed via NBOHCs luminescence at 1.9 eV does not resonantly excite these levels, an internal conversion process being responsible for a transfer between a primary excited defect and NBOHC. These defects, also visible in green luminescence (550 nm) excited by HeCd 325 nm sources (Fig. 4(b)) can be related to ODC in form of silicon clusters similar to $E'_{5/2}$ defects (illustration insert in Fig. 4(c)). These are sometimes accompanied by a PL band at 3 eV. A non identified laser-induced defect LID (Ar$^+$-excited 530 nm PL) is equally observed. This indicates a dose-specific nature and a site-specific spatial repartition of defects mirroring the local morphology and structural environment and the respective strength of bond breaking between soft and strong index changes. At the same time complementary Raman investigations confirm a densification scenario for positive index changes. Particularly for type I these (Figs. 5(a) and 5(b)) indicate a stronger compaction of the glass matrix via the number of densely-packed three-member rings increasing monotonously with the dose as monitored by the D$_2$ peak in the Raman spectrum. A linear relation between the relative D$_2$ magnitude and
the refractive index change value was found, where this gradually increases and then saturates with the accumulated dose.

Several observations can be made at this point. Type I conditions correspond usually to a low subcritical excitation dose, characteristic to low fluences or loose focusing. In the latter conditions, the nonlinear propagation conditions and particularly light defocusing on the mobile carriers impede the achievement of electronic densities surpassing the critical density at the specific laser frequency. Thus the locally deposited energy densities are remaining at a base level. Energy balance considerations question therefore if a phase transition related to a significant increase of temperature (as usually invoked in fictive temperature models) can be achieved in type I traces, putting forward a different factor for the observed refractive index change, namely the concept of “cold” defect-assisted densification. With average kinetic energies in the range of 10-15 eV [12, 33], the relaxation of the electronic excitation cannot drive high temperatures [30, 32], the local heating ($\Delta T \approx 300$ K using standard silica thermal properties) being below the material softening values [30]. In these conditions, as the thermomechanical effects seem negligible, it appears that the laser-generated defects have a determinant effect in triggering structural transitions corresponding to a denser packing.

Thermomechanical effects related to pressure waves, compaction, cavitation, and rarefaction, with signs of low viscosity regions take place in type II traces [14, 22, 23, 30]. These are amounting to the formation and movement of voids, void agglomeration and reshaping as nanogratings. Sub-ns characteristic times were determined for void formation via mechanical rarefaction [14] with local temperatures in the range of the softening values, as calculated in [12] for single
pulse void formation regimes. The high-dose transformations are particularly visible from a dynamic perspective. Time-resolved optical transmission imaging of the single-shot exposed region and post-mortem spectroscopy results for high energy single pulse irradiation are indicated in Fig. 6. We observed a fast decay (<1 ps) of the low excitation wings of the carrier plasmas together with a long living (>1 ns) absorptive core (Figs. 6(a)–6(c)). Further slower dynamics at the matrix level due to stress release was indicated on microsecond scale [34]. The carrier excitation and the observed relaxation with the different dynamics levels determine a specific electronic signature in the modified regions (Figs. 6(d)–6(f)). The fast electronic decay, presumably via exciton trapping [15] leaves behind a zone rich in NBOHC (Fig. 6(e)), although no visible index modification appears. In the slow decay region, indicative of a low viscosity zone and even of a temperature-driven phase transition, we note the appearance of voids and interfaces accompanied by the release of pressure waves. Here the presence of ODC can be recorded (Fig. 6(f)). This indicates a strong morphological and electronic alteration with severe bond breaking and even observation of oxygen radicals [28, 30]. In multishot regimes ($N > 1000$) in comparison with the single shot, the emergence of a void merging zone with the onset of nanogratings (Fig. 3) leaves a particular absorption signature, with strong scattering from the nanogratings region and plasma excitation in the high index apex region.

Due to its nonlinearity, the laser-induced modification has a strong dependence on intensity and therefore prone to be particularly sensitive to time/spectral-domain pulse shaping techniques and pulse envelopes [12, 29, 35]. Intensity design can facilitate type I to type II transitions (as it was seen in Fig. 3) as well as void appearance and confinement of interaction on the smallest scales, as the incoming energy rate is synchronized with the dynamic material response. The pulse time envelope can influence either the absorption conditions or the relaxation characteristics of the laser-generated heat source, both the thermal or mechanical relaxation channels or the geometry of the source. A review of possible time excitation effects was recently proposed [35]. One particularly important aspect for bulk photointeractions, the nonlinear propagation in the volume and the timing of plasma formation with its impact on light scattering or energy deposition create the conditions for a user-defined balance between ionization mechanisms. Better energy confinement even below the diffraction limit and the achievement of higher temperature and pressure conditions in the interaction region were seen for ps envelopes [12, 29, 36, 37]. This, as it will be seen in the following, has consequences on the laser-induced modification morphology. The examples below focus on the nanostructuring phenomenon and its impact in optical functionalization.
3.2. Nanogratings control via excitation levels

The dose dependence of the structural modification indicates that control via electronic excitation may be possible for the nanostructured patterns. It has been discussed before [36] that, upon propagation, a stretched pulse can localize more efficiently the energy as the plasma defocusing effect stays low. This has consequences on the topology of the phase objects as void-like rarefaction zones can be achieved on larger scales, influencing also multipulse topologies. We recall that multipulse exposure can develop regular nanogratings potentially seeded by an initial roughness of the modified region via void merging [27] and a question can be asked if these nanogratings are not dependent and therefore controllable via the excitation level. It will be shown below that this is indeed the case. An open loop based temporal shaping procedure with feedback derived from in-situ UV diffraction on the nanogratings was performed, with details given in Ref. [38]. A certain tunability of the nanogratings period can be achieved (270–210 nm), with the smallest period for pulses around 1 ps [38]. The output of the controlled excitation experiment is discussed below.

A pulse control unit based on spectral phase modulation permits tailoring the time envelope of the output pulses [39]. The pulse elongation was obtained by upchirping the pulse using programmable second-order dispersion with variable GVD parameters. A second pulse derived from a ps microchip laser operating at 355 nm was focused on the traces at the incidence angle $\alpha$, closed to Bragg diffraction conditions. The real-time diffraction pattern, equivalent to a Fourier transform of the diffraction source, is recorded on a fluorescent paper screen backing.
Fig. 7. Tunable ultrafast laser-induced nanogratings periods as a function of the pulse temporal shape visualized via in-situ UV diffraction on periodic patterns. (a) Experimental concept. (b) Diffraction shift for exposure at various pulse durations, equivalent to period tunability. A period variation from 270 nm to 210 nm is achieved between the shortest fs pulse and the optimal 0.65 ps [38].

the sample and, after IR filtering, further imaged on a charge-coupled CCD camera. Figs. 7(a) and 7(b) resume the experimental concept and the diffraction results. The observable spatial shift of the diffraction pattern as the pulse duration varies is equivalent to a tunability of the nanogratings period of tens of nm. Nonlinear pulse propagation calculations indicate a maximum electronic excitation density in these conditions that deliver the smallest period (210 nm) for pulses around 0.7 ps [38]. The driving factor appears to be related to increasing carrier densities due to nonlinear energy convergence in the excitation region, as for longer pulse duration plasma defocusing is less efficient and energy can concentrate more efficiently. Optimal pulse durations can therefore be defined, balancing the efficiency of excitation and the nonlinear confinement. The subsequent influence in facilitating void formation (see e.g. Figs. 3(f) and 3(g)) allows for the development of extended nanoroughness domains upon multiple exposure, derived from a pulse-dependent effective accumulation dose and a morpho-dimensional effect.

3.3. Laser-photoinscribed optical functionalities

The consequences of understanding and control of refractive index changes are multiple. The laser-induced refractive index changes and structural modifications and their modulability have had dramatic consequences on the field of optical functionalization either for waveguiding components or data storage [2, 3]. The efforts were concentrated on several directions. Among them, the most efficient focused on optimizing the material response [19], on design of optical circuitries [4] or source and beam engineering for high efficiency programable automated fabrication with optimal interaction [36, 40, 41].
The possibility to achieve smooth or controllable nanostructured domains has several consequences for the optical functionalities. The local refractive index change is at the base of a range of applications including fabrication of optical elements and optical guiding [1–9]. The relatively smooth low index contrast ($10^{-4}$–$10^{-3}$) of type I structures with dimensions in the micrometer range allows efficient light guiding with losses below 1 dB/cm. A normalized frequency around unity indicates that guided modes are delocalized and that concepts based on evanescent coupling in waveguide bundles can be particularly interesting. Void-like modifications on the other hand can localize structural modifications on sub-micron domains [22, 29], putting forward concepts of high density data storage.

As in processing applications the fabrication efficiency is of interest, photoinscription throughput can be upgraded using programmable beam engineering and parallel approaches. Examples of type I guiding with optical division function, subject to fabrication by programmable beam splitting, or dot arrays via on-axis multipoint focusing are given in Figs. 8(a)–8(d). These are derived via pulse multifocus engineering in the focal plane or, respectively, via truncation-induced diffraction and axial multipoint focusing [29, 40, 42]. Figs. 8(a) and 8(b) show dose-dependent type I waveguides which can be arranged in 3D arrays, evanescently splitting the optical signal upon injection in a central guide. Figs. 8(c) and 8(d) show axial multiplexing of focusing points caused by multiple interferences of reoriented wavevectors of truncated beams. The local intensities are sufficiently high to generate series of dots along the beam propagation axis.

In terms of optical functionalities, the capability of low-loss guiding of type I traces can be combined with the anisotropic nature of type II nanogratings. The electric field dependent scattering of these subwavelength periodic patterns leads to additional polarization functions. Relying on evanescent coupling in guides arrays and bundles different functions were demonstrated such as photonic lattices, spectral demultiplexing, or optical switching [1–9, 26, 40]. We indicate below an example that couples low-loss guiding with large mode area transport and
polarization scattering arising from orientational elastic scattering on the nanoplanes. A large mode area guiding trace combining type I multicore traces in hexagonal arrangements and type II scattering defects is presented in Fig. 9 together with its optical performances (polarization selective guided modes), indicating that a combination of optical functions can be achieved in one system [43].

4. Conclusion

In conclusion, we indicated structural and electronic transformations related to type I and type II photoinscription domains, with spatial defect segregation between non-bridging oxygens and oxygen deficiencies. We also indicated different dynamics of electronic excitation, either fast (sub-ps) or slow (ns) as a function of the initial excitation level, leaving behind specific optical, structural, and electronic transformations. In addition we demonstrated control options in nanogratings tunability via envelope time design and suggested polarization sensitivity laser photowritten optical devices with various optical functions.

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