Light Induced Self Inscription (LISI) in Organo-silica Nanocomposite Network Glasses

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ABSTRACT

We describe optical self-action effects that lead to light induced self-inscription (LISI) in nanocomposite hybrid inorganic-organic glassy media. The LISI response is quasi-solitonic in nature and results in the writing of a permanent nanocomposite waveguide within a waveguide. Accordingly, we describe LISI in sol-gel derived photosensitive glasses containing nanodispersions of zirconia. Waveguiding at 488 nm proceeds with simultaneous self-inscription, and permanently inscribed nanocomposite waveguides can be revealed by wet etching. Under certain conditions, self inscription becomes chaotic, and filamentation is observed. In other cases, periodic beat patterns can be imaged. A counterpropagating beam set-up allows simple optical devices like crosses and y-junctions to be created, and in certain cases periodicity can be extended to wrinkle patterns in the nanocomposite under control to the self-inscribed waveguide structure.

Keywords: LISI, self inscription, nanocomposite waveguide, filamentation, pattern formation, spatial soliton

1 BACKGROUND

Wave instabilities are remarkable phenomena that result when an intense laser beam induces a refractive index change while propagating in a medium. Self-focusing, self-trapping and soliton formation are among the unusual optical self-action effects that have been extensively studied [1]. Self-focusing occurs when light causes a change in the (nonlinear) refractive index, Δn, that resembles the intensity profile of the light. This change induces an optical lens that causes the beam to focus (narrow) along its path. When self-focusing exactly balances diffraction, the beam is self-trapped and a spatial soliton is formed. In the past decade, the study of spatial solitons has intrigued researchers in optics and nonlinear phenomena; but while Kerr and photorefractive nonlinearities have long been associated with solitons arising from transient self-action, only recently has soliton-like behavior manifested itself in new ways in organic and inorganic media that exhibit a permanent Δn [2,3] We ascribe the permanent Δn to Light Induced Self Inscription (LISI) in the latter media. Since the Frisken experiment in UV cured epoxy [4] LISI has been observed across a diverse material base [2,3]. LISI is important because it raises new questions about its origins in matter-photon interactions, its interpretation and its potential applications. Self-action in LISI differs from self-inscription in quadratic and Kerr media where the effect is instantaneous, transient and non-cumulative. Similarly, effects in photorefractives are nonlocal by virtue of freely diffusing inhomogeneous space-charge distributions. Nevertheless, we have observed that LISI is accompanied by filamentation, periodic beating, self-trapping, and soliton-like behavior reminiscent of transient media [5].

We have reported how mode and polarization state selected guided waves from laser excitation will simultaneously write a permanent waveguide-fiber-on-a-chip in hybrid organic-inorganic nanophase silica network composites (Figure 1) [5,6]. We subsequently elaborated our findings to establish how Waveguide Raman Spectrosc-

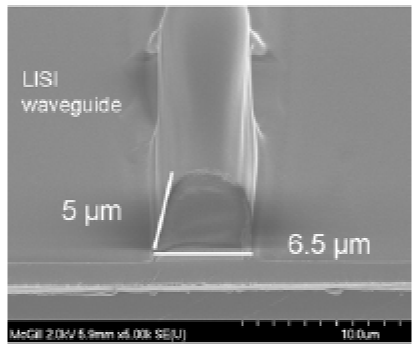

Figure 1: LISI nanocomposite waveguide from hybrid sol gel glass revealed by organic solvent wet etching. Waveguides have been fabricated up to 6 cm in length.

opy (WRS) can be used as an optical “read out” of anisotropy in the polarizability tensor to provide molecular insight into self-organization [7]. Singular features of our approach are our ability to interrogate the vibrational structure of LISI waveguides in situ, and to obtain permanent 3D waveguides and simple devices by direct organic solvent wet-etching. In a recent preliminary report, we expanded the technique to create simple optical devices (optical crosses, junctions and interconnects) on silicon chips [5]. Moreover, we showed for the first time that counterpropagating self-inscribing beams undergo mutual self-trapping in nanocomposite hybrid organic-inorganic sol-gel network glasses [5]. Surprisingly, the literature on permanent LISI has focused narrowly on studies in commercial liquid resins, chalcogenide and germanosilicate glasses. Since LISI is locally linked to an increase in refractive index via bond breaking and making, it makes sense to have a common underlying photochemistry to link different materials classes. We do this by incorporating well-defined crosslinking agents into our media. Our approach avoids the ambiguities of interpretation associated with writing events that rely on creating ill-defined defect centers by direct optical damage. Since we design our

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materials as "negative photoresists" we obtain media that both guide light and record a permanent 3D image of the LISI event. Relief imaging is a feature of our chemistry that is also unique in the literature on LISI in solid media and allows more leisurely spectroscopic, optical and topographical analysis of the waveguide features. In this paper we describe the LISI experiment in photosensitive nanocomposite slab waveguides from sol gel-derived organically modified silica glasses. Smooth-walled quasi-cylindrical fiber-on-chip structures are straightforward to obtain. We further show that the materials properties and the self-writing conditions can be tuned to directly self-inscribe waveguides with periodically-modulated edge walls. Finally, we discuss the impact of material design and exposure conditions on the stability of self-inscription process.

2 EXPERIMENTAL

2.1 Sol Formation

The details of the synthesis of the organically modified silica network glasses are described elsewhere [8]. A sol is synthesized by hydrolyzing a [3-(methacryloyloxy)-propyl]trimethoxysilane monomer under acidic conditions and incorporating it with a pre-chelated zirconium (IV) propoxide network modifier. The latter is thought to form clusters of methacrylic acid surface-chelated zirconia in the organically modified matrix of the siloxane. After ageing, the sol was photosensitized with between 0.7 to 1.2% w/w of bis (η-5-2,4-cyclopentadien-1-yl) bis [2,6-difluoro-3-(1H-pyrrol-1-yl) phenyl]titanium (Irgacure 784, Ciba-Geigy, Switzerland). Alternatively, the sol was photosensitized with titanocene dichloride. The sol was then filtered and spin-coated onto a silicon wafer faced with a 2 micron thick thermal oxide SiO_2 layer. After thermal pre-treatment, the 488 nm line of a cw Ar+ ion laser was prism coupled in the film. After 15 min exposure, a 7-10 cm self-inscribed waveguide structure was grown. The unexposed material was wet-etched with a isopropanol.

3 RESULTS AND DISCUSSION

3.1 Principle of the Experiment

LISI depends primarily on the creation of a permanent Δn in the medium. The principle of the experiment is idealized in Figure 2. With a coupling prism, an embossed or an etched Bragg grating, we excite a desired mode and polarization state of the waveguide. The guided wave bleaches a photoinitiator in its path. Radicals or cations that are produced then react with crosslinker molecules covalently bound or dissolved in the film. We believe that crosslinking densifies the matrix, increasing n, which causes the beam to focus and narrow. This is the "write" process. We simultaneously collect Raman photons scattered from the waveguide to monitor LISI at the chemical functional group level [7,8]. Our Waveguide Raman Spectroscopy (WRS) experiment is unique in the

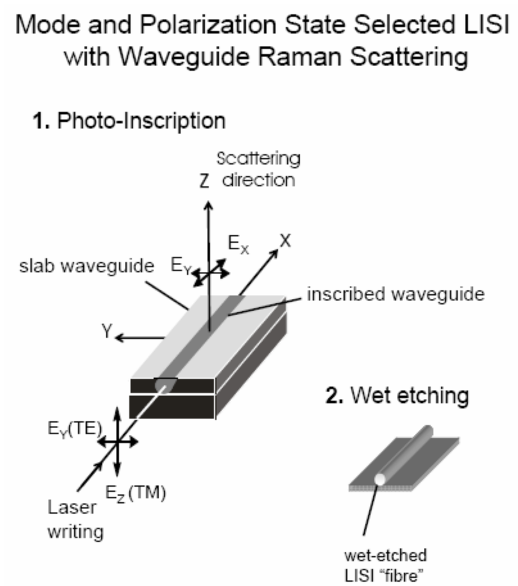

Figure 2: Principle of the LISI experiment with simultaneous spectroscopic read-out.

LISI literature. This is a guided wave "read" experiment. After optical inscription, the film may be wet-etched with an organic solvent to reveal the LISI waveguide (Figure 2).

3.2 The Nanophase Organosiloxane Composite

The nanophase composite is prepared via the generic reaction $xR_lE(OR')_{n-l} + yE(OR')_m + zH_2O \rightarrow R_qEO_p + wR'OH$. R is a latently reactive functional group (vinyl or acrylate) covalently bound to an oxide forming p-block element, E (usually Si). When R is photoreactive, we obtain a hybrid organic-inorganic. The zirconium is included to adjust the refractive index of the composite to achieve waveguiding. A principal advantage of the hybrid glass is that it permits molecular-level control over macroscopic expressions of physical and chemical properties that are important for photonic devices. This gives the device designer an attractive generic silica-based medium that allows rapid prototyping. The trifunctional $RSi(OCH_3)_3$ reduces glass network connectivity and mechanical stiffness. Reduction in the mechanical stiffness of the network promotes capillary stress-induced collapse of the gel network during drying. This is reflected in enhanced relaxation rates and lower densification temperatures for the glasses. Overall, the photo-crosslinked glass can be viewed as kind of "molecular alloy" of inorganic silica and an organic oligomer or polymer.

3.3 Guided Wave Self-Inscription with Periodic Patterning

When the laser beam is coupled into a multimod photosensitized waveguide (~6 μm thickness), the propagating mode appears as a bright yellow-orange streak. The streak slowly grows in the forward direction, away from the coupling prism, across a distance of 7-10 cm in a few minutes. Exposure is maintained for approximately 15 min to consolidate the evolving self-inscribed structure. The unexposed material is wet-etched and a straight fiber-like structure is revealed on the substrate. A scanning electron micrograph of such a self-inscribed fiber is shown in Figure 1.

During LISI, photolysis of the Irgacure 784 initiator generates free radicals that initiate the polymerization of the pendant methacrylate side-chains. Radical crosslinking densifies the matrix and raises the local refractive index as the available C=C vinyl groups are converted to short covalent C-C single bonds in the glass. This is confirmed by in situ waveguide Raman scattering from the LISI waveguide [6]. The refractive index increases most along the propagation axis, compensating the linear dispersion of the material. Over time, the profile of the guided laser beam narrows as it self-focuses.

The self-inscription event was imaged with a CCD camera fitted with a 20X magnification long working distance microscope objective. It is evident from Figure 3, that the guiding structure exhibits a periodic modulation along the length of otherwise parallel walls.

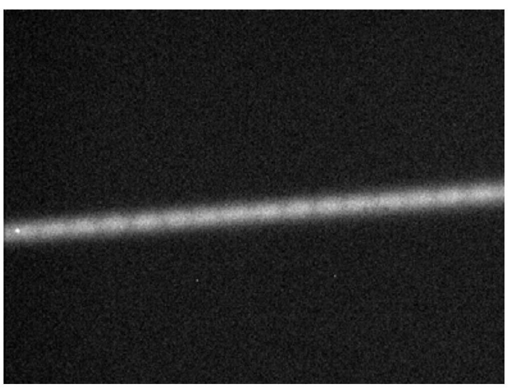

Figure 3: 20X magnification view of the self-inscribing beam guided in a slab waveguide. The waveguide exhibits a periodic beat pattern.

To capture the periodic pattern in a wet-etched self-inscribed structure, we resorted to somewhat different fabrication conditions. We observed that direct optical self-writing of periodically modulated waveguides was achieved more easily in a medium with reduced photosensitivity. For these experiments we used titanocene dichloride as the photoinitiator. With this formulation, 4 to 5 longer exposure times were needed. We note that the resolution of the edge-wall corrugations was cleaner in waveguides supporting only a few modes, typically 3. Wet etching after LISI resolved the physical beat pattern in the waveguide. This is shown in Figure 4, where an atomic-force micrograph is re-

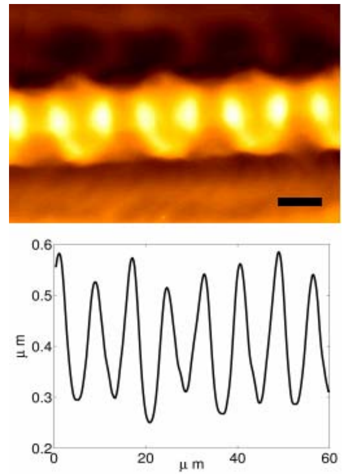

Figure 4: Atomic force microscope image of a wet-etched self inscribed waveguide. Physical features of the periodic pattern are clearly evident. Height to trough depth is on the order of 0.3 μm, with a wavelength of roughly 8μm.

produced. The wavelength of the beating is about 8 μm. This experimental result is reproduced in calculations. The beat lengths for each film thickness were calculated using a bisection method, assuming that beating occurs between the zeroth and second (even order) modes. Figure 5 shows that a film approximately 0.8 μm thick will pro-

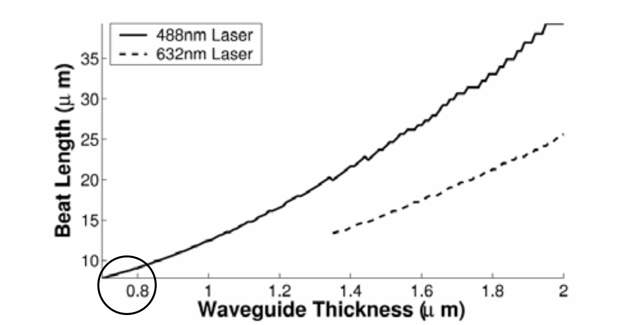

Figure 5: Beat length as a function of waveguide thickness for different wavelengths. Beat lengths are shorter for thinner films at shorter wavelengths.

duce optical beating with a period of about 8 μm at a wavelength of 488 nm. This corresponds almost exactly to the conditions of our experiment, where films were approximately 0.85 μm thick. At longer wavelength, thicker films are required to support the minimum of 3 modes. For

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this reason, the starting beat length is much larger. As anticipated by the theory of Snyder et al. [9], the increased refractive index in the mature self-written waveguide means that it can support additional modes, where the even order species can beat optically to modulate the density and stress in the waveguide. This is the first physical evidence of recording periodic patterning in a self-written waveguide.

Under some conditions the guided wave behaves chaotically and breaks up into filaments, as shown in Figure 6. The original self-inscribing beam remains the brightest filament and still shows a periodicity. The relative optical

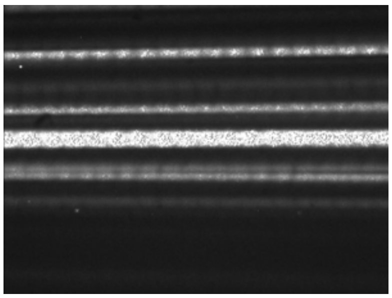

Figure 6: Filamentation of the principle waveguide (brightest streak) during LISI.

power diverted into the filaments varies in time: filaments can form or disappear altogether. This record of chaotic behavior is persistent and is permanent in terms of numbers of filaments when the recording process is halted at different times. Filament breakup and fusion can occur, so the number of filaments and their width and spacing depends on the recording time; different recording times give rise to somewhat different patterns of filaments. In fact, the present experimental work gives a “freeze frame” direct visualization of many of the dynamical processes of filamentation including self-focusing, group velocity dispersion, intensity clamping, filament fusion, breakup and multiple filament competition for the first time using LISI. Interesting is the persistence of periodic features in the filaments, and many of the “mature” filaments appear to have the same beat lengths. This may point to a certain universality of filamentation – mature filaments have the same properties depending on the probe experiment. We note that filamentation with periodicity has been observed in liquid crystal media owing to a nonlinear effect that is optically induced in the director reorientation [10]. The periodic modulation observed in this case is transient.

Like photosensitive direct writing, LISI can create straight waveguides and optical components such as taps, couplers, tapers, crosses and splitters directly in buried planar waveguides [5]. Because nanocomposite glass films formed by spin coating are dissipative structures under stress, they respond to perturbations by recruiting wrinkle patterns that show different length scales and patterns under partial control of the LISI process. Self-inscription of the optical cross shown in Figure 7a gives rise in Figure 7b to a

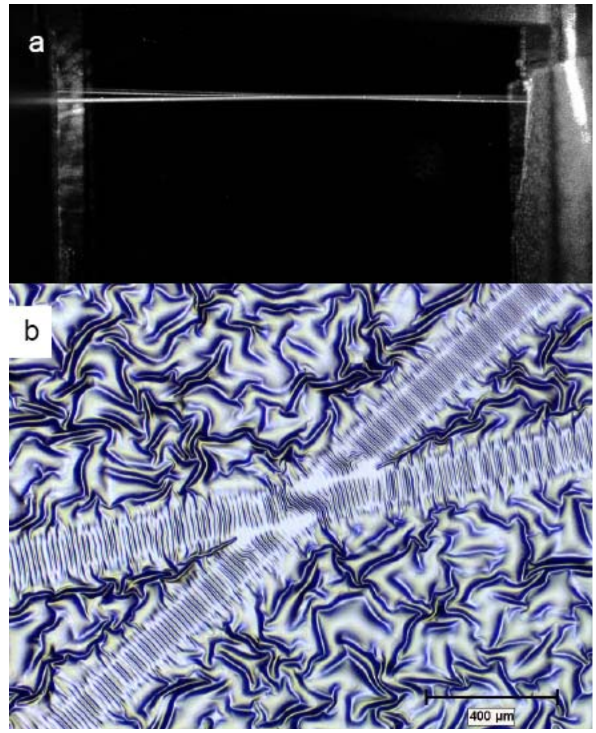

Figure 7: a) Optical cross formed by counterpropagating beam LISI in nanocomposite glass. b) Periodic wrinkle patterns formed in nanocomposite glass optical cross after partial wet-etching.

periodic wrinkle texture in the nanocomposite material after partial wet-etching. LISI can be used to control pattern formation through self-inscribed optical device constructs over length scales that vary from the nanoscale through to the mesoscale.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial assistance of the Natural Sciences and Engineering Research Council (NSERC) of Canada for support of this research. Technical work was supported in part by a service agreement between McGill University and Silk Displays.

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