

Multiple Beam Internal Structuring of Poly(methyl methacrylate)

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Spatial light modulator addressed with computer generated holograms is used to diffract femtosecond laser pulses into > 15 parallel beams and focused simultaneously inside poly(methyl methacrylate) (PMMA) for high throughput 3D refractive index modification. Uniform modification throughout the structure is demonstrated and used to create a $19 \mu\text{m}$ pitch, $5 \times 5 \times 3.5 \text{ mm}^3$ thick volume grating in < 50 minutes with first order Bragg diffraction efficiency $> 65\%$. Thick volume phase gratings are created by carefully stitching filamentary modifications. PMMA shows a remarkable time dependent Δn , related to the photochemistry during and after exposure.

DOI:10.2961/jlmn.2012.02.0014

Keywords: femtosecond laser, volume grating, spatial light modulator, PMMA, refractive index modification

1. Introduction

Femtosecond laser micro-machining inside transparent optical materials (induced by non-linear absorption) is now well established for the creation of 3D photonic devices. These include passive and active components such as waveguides [1], gratings [2, 3], couplers, splitters [4-6], amplifiers and lasers [7]. Poly(methyl methacrylate) (PMMA), in particular, is attractive due to favourable characteristics such as optical transparency, processability and low cost. Bulk Δn modification of pure PMMA is of interest because of the potential of creating useful devices for clinical, biological and chemical applications that can be integrated with lab-on-chip micro-fluidic devices.

For effective femtosecond modification of refractive index in the NIR, short temporal pulse duration $\tau < 120$ fs is advantageous in optical materials since this reduces avalanche ionization relative to multiphoton ionization [8]. While multiphoton ionization creates the seed electrons at the front edge of the femtosecond pulse, avalanche then generates an exponential rise of electron density, and as energy is coupled to the lattice, the material can undergo a phase or structural modification creating a permanent change in refractive index. Above pulse duration $\tau > 150$ fs, optical breakdown leading to voids is more likely. In PMMA, effective Δn structuring at $\tau = 170$ fs pulselength was demonstrated at the NUV wavelength $\lambda = 387$ nm ($h\nu = 3.2$ eV) by reducing the order of non-linear absorption from three to two-photon [2].

High NA > 0.4 is ideal for direct writing of waveguides [1], void formation [3] and micro-channels. For example, Yamasaki et al demonstrated direct fabrication of sub-micro 3D micro-channels in PMMA by femtosecond pulses using a high NA objective (NA = 1.35) [9]. However, at

low NA ~ 0.1 , filamentation occurs, leading to much longer modification depths of around 100-200 μm , useful for producing volume gratings. In addition, at such low NA, spherical aberration from the interface is expected to be negligible, allowing uniform modification up to depths > 5 mm below the interface [10].

At 1 kHz repetition rate, only $\sim 1 \mu\text{J/pulse}$ femtosecond is required to create useful Δn and as pulse energy $E_p > 1$ mJ is typically available, the light utilisation factor is $< 0.1\%$. By using a Spatial Light Modulator (SLM), addressed with optimised Computer Generated Holograms (CGHs) to create a large number of near uniform diffracted beams of the requisite pulse energy, this efficiency is increased by more than an order of magnitude, reducing the fabrication time while allowing arbitrary parallel processing [11-13].

In this paper, particular attention is paid to control of filamentation hence minimizing non-uniformity during inscription while carefully stitching filamentary modifications in 3D. Consequently, thick volume phase gratings can be inscribed at much higher speed.

2. Experimental

The experimental set up has been described elsewhere [14]. Briefly, the output from a Clark-MXR CPA-2010 femtosecond laser system (775 nm, 170 fs pulse duration, 1 kHz repetition rate, 1 mJ) was attenuated and expanded to 8 mm diameter onto a phase only reflective liquid crystal on silicon SLM (Hamamatsu X10468-01, AOI $< 10^\circ$) and a $4f$ optical system was introduced to re-image the complex electric field at the SLM to the back focal plane of the objective. (Nikon, type CFI LU Plan Fluor BD 5 \times , 0.15 NA, $f = 40$ mm, $WD = 18$ mm) while removing the remaining

energetic zero order with a small target near the Fourier plane of the first lens of the 4f system. PMMA substrates (Vistacryl CQ) were optically polished on all sides, mounted on a precision 3-axis motion control system (Aerotech) and diffracted beams were carefully focused > 0.5 mm below the substrate to keep the fluence at the interface below the damage threshold. An effective $NA_{\text{eff}} = 0.1$ was used here.

From the desired intensity distribution at the focal plane of the objective, the corresponding CGH was calculated using the Gerchberg-Saxton algorithm within an interactive LabView environment was applied to the SLM and the calculated phase pattern (8-bit greyscale) was observed on a separate monitor [15].

Intensity non-uniformity between spots was minimized by introducing slight random displacements of the required spot pattern in the writing direction, which minimizes the effect of overlapping ghost beams while maintaining fixed pitch Λ [14].

A schematic diagram, shows the basic geometry used in parallel processing, Fig.1.

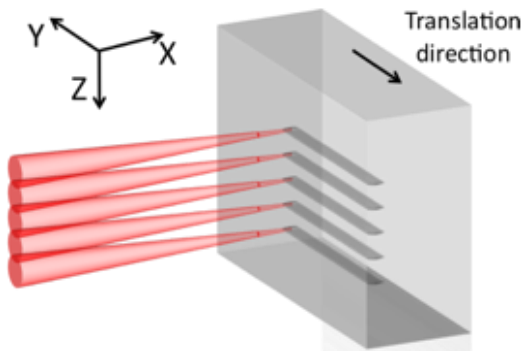


Fig.1 Transverse geometry for parallel writing grating inside PMMA

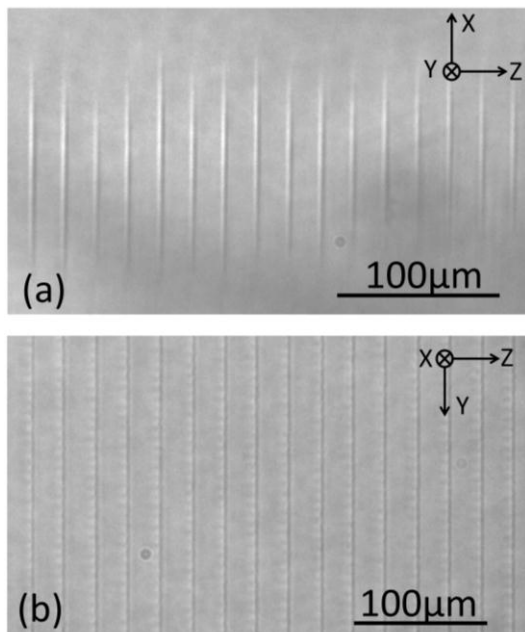


Fig. 2 (a) Cross section and (b) front view of the modifications written by 16 parallel beams.

3. Results and Discussion

Δn modification of PMMA without optical breakdown at 775 nm, 170 fs with 16 parallel beams with a period $\Lambda = 19 \mu\text{m}$ is shown in the optical micrographs of Fig. 2 (a, b). Pulse energy $E_p = 0.6 \mu\text{J}/\text{beam}$ and transverse scan speed $s = 1 \text{ mm}/\text{s}$ were used and each modified region was scanned once only.

With optimized CGH, the with measured filament length $l = 109.9 \pm 6.1 \mu\text{m}$ (1σ). With this optimisation, Fig. 2 (a, b) shows front and cross sectional views of 16 near uniform lines written simultaneously within PMMA. An overlap of filaments by a distance of $10 \mu\text{m}$ ($\sim 10\%$ overlap) was found to be satisfactory to achieve continuity and uniformity.

The filaments are $4 \mu\text{m}$ wide and $l \approx 110 \mu\text{m}$ in depth. The relatively long modification depth is due to the dynamic balance between Kerr self-focusing and the defocusing effects of the electron plasma generated during the ionization process.

By scanning this 16 beam optimised intensity distribution in the transverse (+Y) direction with Z-axis increments ΔZ of $304 \mu\text{m}$ ($16 \times 19.0 \mu\text{m}$), then offsetting in the axial (X) direction with ΔX of $\sim 100 \mu\text{m}$ (deepest first), a thick grating (35 layers) with dimensions of $5 \times 5 \times 3.5 \text{ mm}^3$ thick was created in about 50 minutes. A synchronised fast mechanical shutter ($\tau_r \approx 3 \text{ ms}$) controlled from within the motion control software avoided unwanted exposure of material.

The grating efficiency at the Bragg angle $\theta_B = \arcsin(m\lambda/2\Lambda) = 0.80^\circ$ ($m = 1$) shows a remarkable temporal dependence, Fig. 3, developing over a period from hours to days and saturating, in the case of first order to $\eta_{\text{max}} = 66\%$ after one week. The grating thickness parameter is given by $Q = 2\pi\lambda L/(n\Lambda^2)$, where L is the grating thickness (3.5 mm) and $n = 1.49$ is the refractive index of the bulk PMMA hence $Q \approx 22$ so that the grating is a thick volume grating ($Q > 10$) [16], and hence should show a high angular selectivity, well demonstrated in Fig.3.

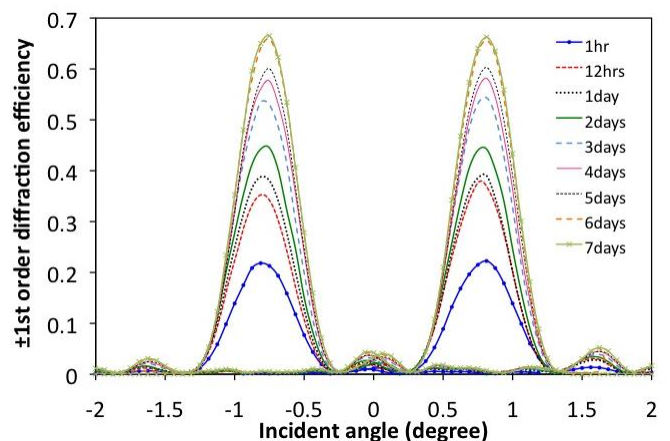


Fig. 3 First order diffraction efficiency with time of 19 μm pitch volume phase grating ($5 \times 5 \times 3.5 \text{ mm}^3$) written by 16 uniform beams.

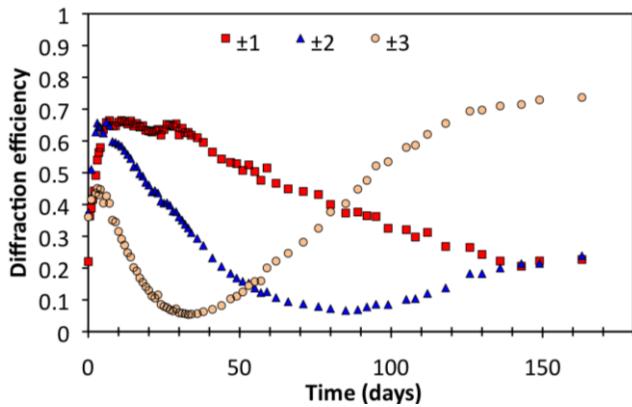


Fig. 4 Diffraction efficiency at the Bragg angles ($\lambda = 532$ nm) for first to third orders showing temporal behaviour over 5 months.

This temporal development has a number of sources. The primary photochemical product is monomer MMA [17] and the MMA molecules, soluble in PMMA can diffuse out into the unexposed regions between the grating lines. Monomers present in the bulk reduce the refractive index there. In exposed regions, cross linking which can pull molecules together may also occur leading to increasing local density hence Δn modulation alters both temporally and spatially. The photochemical reaction produces lower molecular weight fragments with unsaturated end groups which also give a positive refractive index change. It has been shown that heating bulk PMMA samples after femtosecond laser exposure can accelerate grating development, which may also support MMA diffusion as the mechanism for the temporal behaviour [18]. Stress relaxation may also be important over this timescale. More stable structures can be expected at shorter pulselength $\tau \approx 100$ fs in the NIR where multi-photon ionisation increases relative to impact ionization or at shorter NUV wavelengths [2, 8].

The measured width FWHM of the angular Bragg envelope (Fig. 3) $\Delta\theta_{\text{FWHM (exp)}} = 0.47 \pm 0.02^\circ$ while first order Kogelnik theory for holographic volume gratings [16] gives an expected half width $\Delta\theta_{\text{FWHM}} \approx \lambda/L \approx 0.31^\circ$. Holographic gratings have a harmonic refractive index modulation $\Delta n = \Delta n_0 \cos(2\pi z/\Lambda)$ while the index modulation profile here involves discrete modified regions. The expected first order diffraction efficiency can be estimated from $\eta_{\pm 1} = \sin^2(\pi \Delta n_0 L / \lambda \cos \theta_b)$ where Δn_0 is the amplitude of modulation and θ_b is the first order Bragg angle [16].

From the measured maximum first order efficiency $\eta = 66\%$ the corresponding $\Delta n_0 = 4.6 \times 10^{-5}$, quite modest but not unexpected at the temporal pulselength of 170 fs at 775 nm. The high efficiency here has been achieved as a result of the uniformity and thickness of the grating. Fig. 5 shows the first order diffraction efficiency measured over seven days and the inferred amplitude modulation Δn_0 . Fig. 6 demonstrates efficient Bragg diffraction at 1st to 3rd order when passing the coherent output beam from a Coherent Verdi ($\lambda = 532$ nm).

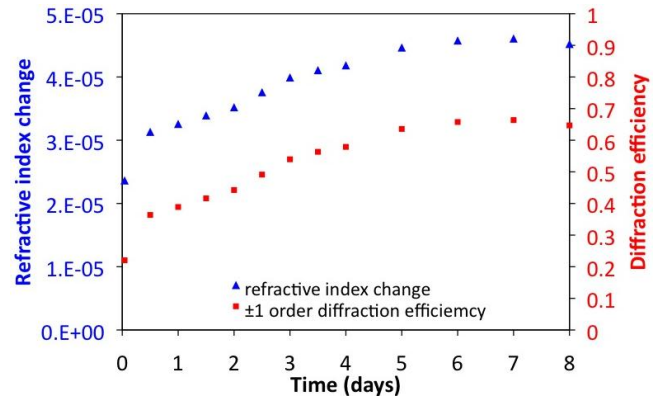


Fig. 5 First order diffraction efficiency with time over first seven days and inferred refractive index modulation Δn_0

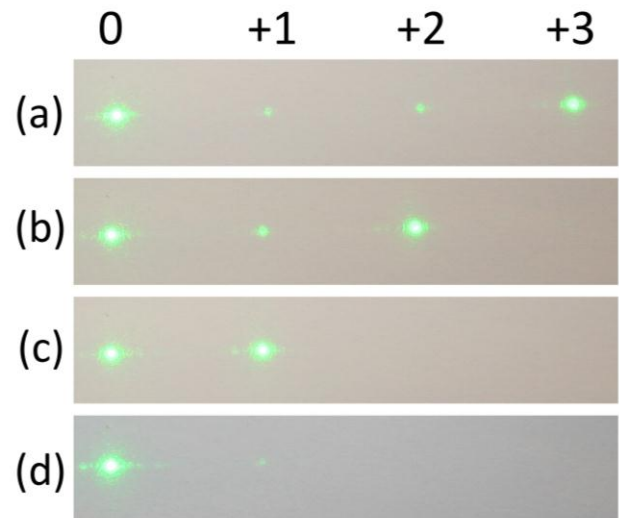


Fig. 6 Bragg diffraction at (a) 3rd (b) 2nd (c) 1st and (d) 0 order from thick volume grating at $\lambda = 532$ nm

4. Conclusions

Highly parallel diffractive writing of uniform Δn structures in PMMA was demonstrated by combining 775 nm, 1 kHz, 160 fs pulses with an phase only SLM addressed with CGH's giving a throughput gain $G = 16$, a potentially useful step in the high speed production of 3D optical photonic components. The uniformity of filamentary modification is achieved by minimizing diffractive intensity modulation through CGH optimisation while limiting filamentary modifications to $\sim 110 \mu\text{m}$ lengths at $\text{NA} = 0.1$, then carefully overlapping axial filaments to produce a continuous modification. Consequently, thick, high quality volume phase gratings (5×5 mm, 53 lines/mm) with 3.5 mm thickness and $\eta_b = 66\%$ first order diffraction efficiency has been produced at high speed and a refractive index modulation $\Delta n_0 \approx 4.6 \times 10^{-5}$ is inferred. Temporal changes in refractive index are observed after material inscription, probably related to the primary photoreaction product, most likely monomer MMA which diffuses into the bulk over periods of days to weeks since monomer MMA is soluble in PMMA. Monomer present in the bulk reduces the refractive index there while exposed regions may also suffer cross linking, increasing the refractive index [17].

Acknowledgments

This work was supported by the UK North West Development Agency under grant N0003200. The authors are grateful to Prof. Miles Padgett and Dr. Jonathan Leach of the University of Glasgow for providing the SLM control software and Hamamatsu Photonics for supplying the SLM.

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(Received: June 17, 2010, Accepted: April 17, 2012)