

*Rapid communication***Holographic recording using two-photon-induced photopolymerization**

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Abstract. Molecular excitation via the simultaneous absorption of two photons can lead to improved three-dimensional control of photochemical or photophysical processes due to the quadratic dependence of the absorption probability on the incident radiation intensity. This has led to the development of improved three-dimensional fluorescence imaging, optical data storage, and microfabrication. The latter of these involves the fabrication of three-dimensional structures using a spatial variation in the incident intensity within a photopolymerizable resin. In the past, the translation of the focal plane of a tightly focused laser beam was used to induce localized photopolymerization and fabrication of three-dimensional structures. Here we report the first successful demonstration of large-area patterning via ultrafast holography-based two-photon polymerization of a commercially available optical resin and a large two-photon cross-section dye (AF380). This opens tremendous possibilities for the wide-spread use of two-photon absorption for the three-dimensional control of photoinduced processes.

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Recently, the ability to fabricate 3D optical storage devices and ornate 3D microstructures has been demonstrated using two-photon induced photopolymerization (TPIP) [1]. The 3D lithographic microfabrication presented in this reference possessed increased intricacy compared to the TPIP microfabrication work presented in previous reports [2, 3]. This substantial increase in microfabrication complexity was made possible by using chromophores with increased two-photon cross-sections (σ) in conjunction with the confinement of the two-photon absorption to a volume on the order of λ_0^3 , where λ_0 is the wavelength of incident radiation [4]. However, as with previous work on two-photon-based optical data storage [5], it was still necessary to sequentially scan a series of extremely short (100–150 fs), high-peak-power

(< 200–300 μ W) laser pulses in a tightly focused single-beam geometry to cross the TPIP initiation threshold. It is apparent that the synthesis of chromophores with even larger two-photon cross-sections will unleash dramatic improvements in the capability and performance of a variety of two-photon absorption applications, including optical limiting [6, 7], nondestructive imaging [8], data storage [9], low-energy photocuring [10], and three-dimensional microfabrication [11, 12].

Traditional, one-photon-induced polymerization has been well studied and has become an integral part of high-precision processing, such as microelectronic manufacturing, rapid prototyping via stereolithography, and MEMS manufacturing [13]. Two-photon-induced polymerization has been studied to a lesser extent and offers strong promise as a method for the fabrication of 3D sub-micron structures including 3D optical data storage devices and photonic band-gap structures [14]. The initiation of both types of polymerization relies upon a photo-induced molecular excitation and subsequent generation of an initiating species.

We have been exploring the use of two-photon chromophores for optical power limiting, [6, 15] as well as for a number of other applications [16]. Over the course of this investigation, we have been successful in preparing chromophores with some of the largest reported σ values [6, 16, 17]. These large σ value chromophores allow us to explore alternative, non-focused laser geometries for TPIP microfabrication. We show for the first time the microfabrication of a TPIP-based structure by using a holographic technique (HTPIP). Specifically, we recorded a diffraction grating by combining two femtosecond pulses of near-infrared light. This technique opens the possibility of performing bulk, polymer-based 3D lithography instantaneously and represents a dramatic advancement from the single-beam, translation-stage-based TPIP processes currently in use.

1 Experimental details

1.1 Materials

AF380 represents one in a series of aromatic heterocyclic donor–acceptor chromophores consisting of π -electron-do-

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nating and π -electron-accepting moieties separated by a conjugated aromatic core. The synthetic details will be published elsewhere [18]. AF380 was selected on the basis of its large cross-section ($2.9 \times 10^{-21} \text{ cm}^4/\text{GW}$) and strong up-converted luminescence centered at 500 nm. NOA 72TM is a commercially available free radical photopolymerizable thiolene optical adhesive which can be cured with light ranging in wavelength from 315 to 450 nm via photoinitiators with peak absorptions at 320, 365, and 420 nm [19].

1.2 Thin-film fabrication

Thin films were fabricated by spin-coating a 0.4 wt. % blend of AF380 in NOA 72 onto polystyrene and glass slides using a Solitec 5110-C/T spincoater. To ensure solubility and dispersion of the AF380 within the NOA 72 matrix, the chromophore was dissolved in a small amount of benzene prior to blending ($\sim 5\%$ benzene by volume in final solution). The NOA 72 was passed through a 2- μm filter prior to mixing with the chromophore. The final solution was filtered with a 0.45- μm syringe filter immediately prior to spin coating. The films were about 10 μm thick as determined by SEM cross-section.

1.3 SEM, AFM, & Optical parameters

Electron microscopy was performed on a Leica 360FE scanning electron microscope. Samples were coated with a 10- \AA layer of tungsten before imaging. AFM analysis was performed on a Digital Instruments MultiMode atomic force microscope operated in tapping mode. Optical microscopy was performed on a Nikon Optiphot microscope in transmission mode and captured using an integrated 35 mm camera.

1.4 Z-scan analysis

A standard Z-scan experiment was performed on the AF-380 chromophore in tetrahydrofuran (THF) to measure the two-photon absorption cross-section. Details of this experiment are described in the literature, therefore no description is given here [20]. The experimental parameters for the scan were a beam waist of 130 μm , pulse width of 90 fs, pulse energies between 2 and 6 μJ , path lengths of 0.2, 0.5 and 1 cm, at a wavelength of 800 nm.

1.5 Optical holographic setup

The optical setup used to write the grating structures was a standard holographic configuration. A Ti:sapphire femtosecond laser system with regenerative amplification was used to generate a bandwidth-limited 90-fs, 950- μJ pulse centered at 800 nm at a repetition rate of 1 kHz. High-intensity, low-dispersion optics were used throughout the experimental arrangement. The spot size was reduced from 1 cm^2 to 4 mm^2 using a pair of thin lenses in a telescope arrangement, and the beam was split in two using a 70/30 ultrafast beam splitter. Each of the two beams was propagated along optical delay lines, one of which was a variable translation

stage with a resolution of 16.6 fs/step. From the optical delay lines, the two beams were incident on the sample plane at an angle of 10° to the normal, subtending an angle of 20° between them. As the spatial extent of each pulse is approximately 30 μm , care must be taken to ensure accurate temporal and spatial overlap. To ensure temporal overlap, a KDP crystal was placed in the sample plane and the translation stage moved until the maximum of the second-harmonic generation signal was determined. This process has the advantage of allowing us to also autocorrelate the pulse at the sample plane. By maximizing the temporal overlap, we were also forcing the two beams into coherence. In addition, both the KDP crystal and the sample holder were mounted on rails to ensure that the interaction plane was identical by sliding either one or the other into the overlapping beams. The energy of each pulse was attenuated using thin neutral density filters, and was measured at the sample plane using a calibrated power meter. The two beams had energies of 120 μJ and 150 μJ . Both the energy and beam size were chosen to give an appropriate intensity in order to initiate the two-photon photopolymerization, as described earlier. Exposure times were varied from 2 to 7 minutes.

2 Results and discussion

The linear absorbance and photoluminescence of AF380 is shown in Fig. 1. From previous experiments, it is known that the one-photon-induced photoluminescence is nearly identical to the upconverted, or two-photon-induced, photoluminescence. As can be seen from this figure, only the most red-shifted initiator is activated by the upconverted luminescence of the AF380. Due to the strong fluorescence observed during two-photon polymerization, the absorption of upconverted fluorescence by the 420-nm centered initiator of the NOA 72 is believed to be the primary means of polymerization as opposed to the direct formation of an initiating species (i.e. radical) from the excited chromophore [1]. From the Z-scan measurements, the two-photon cross-section was calculated to be $2.9 \times 10^{-21} \text{ cm}^4/\text{GW}$ ($\pm 10\%$) by using the

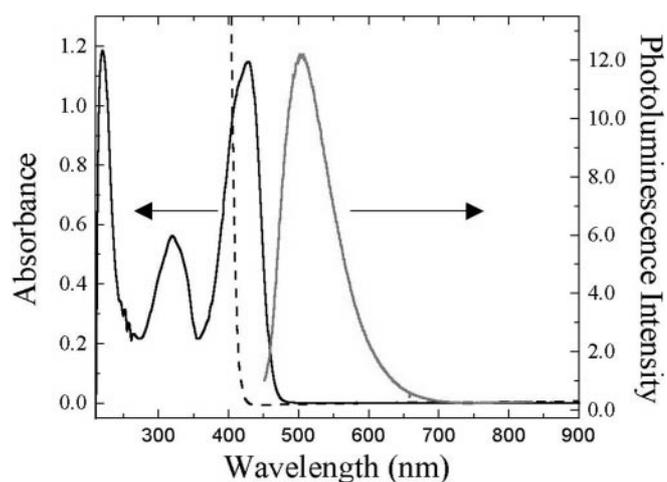


Fig. 1. Linear absorbance of a 10^{-4} -M solution of AF380 in THF (1 cm cuvette, left solid line) and neat NOA 72 (0.5 cm cuvette, dashed). Photoluminescence of AF380 in NOA 72 (right solid line)

standard analytic fit equations. A variation of the pulse energy was also performed and no cumulative effects were observed.

Based on earlier experimental observations employing focused-geometry measurements, it is believed that a threshold intensity exists, above which two-photon photopolymerization can take place. Below this threshold, there is not enough photon density to initiate the process. Additional investigations into this threshold are needed to quantify that value. Using this concept as a guide, one can holographically write an intensity pattern that falls across this threshold value, as illustrated in Fig. 2. The dotted line represents an arbitrary intensity threshold, while the solid line represents an intensity distribution calculated by interfering two 90-fs pulses integrated over the bandwidth. The abscissa is in arbitrary intensity units. Note that the intensity does not fall to zero, because of the bandwidth of the femtosecond pulses. Instead, a beat pattern is observed oscillating about the peak intensity before the pulse is split in two. One would expect that in the regions where the intensity is above the threshold, photopolymerization is initiated, whereas in regions below it is not initiated. It is also expected that some blurring of the features might occur around the intersection of the intensity profile and the threshold due to either propagation of the polymerization and/or material stress caused by the intensity discontinuity imposed for small grating periods. Subsequently, the modulation depth is defined as the vertical distance from the profile maximum

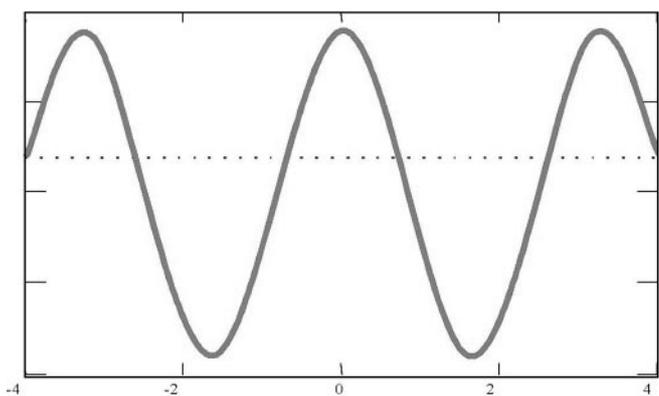


Fig. 2. Intensity profile versus displacement across film in μm . Dotted line indicates arbitrary intensity threshold

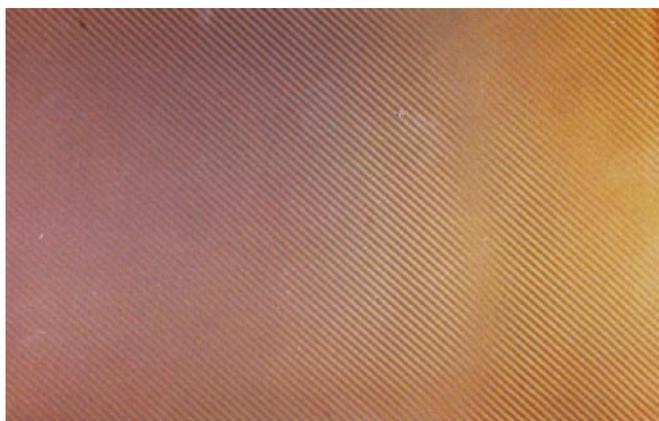


Fig. 3. Optical image of large area two-photon grating. The grating spacing is approximately $3.8 \mu\text{m}$

to the position in the sample where the threshold intensity is crossed. From simple holographic theory, it can be shown that the grating spacing, Λ , for a single-frequency interference pattern is given by $\Lambda = \lambda_0 / (2 \sin \Theta)$ where λ_0 is the wavelength used to write the pattern and Θ is the angle subtended by the two beams. Using the experimental parameters above, a grating spacing of $2.3 \mu\text{m}$ is calculated for a single frequency. Taking into account the entire bandwidth of the pulse, we find a predicted grating period of $3.3 \mu\text{m}$ from Fig. 2.

Using the holographic set-up described above, a series of gratings were written. Figure 3 shows an optical image of a portion of the grating region at $400\times$ magnification. The total area uniformly covered by the grating is 1 mm^2 , representing the central portion of the overlapped pulses. From the absorption edge of NOA 72 shown in Fig. 1, one may speculate that NOA 72 may have a two-photon absorption. However, control films without AF380 failed to produce any type of grating structure or polymerize under the identical experimental conditions, indicating a negligible two-photon absorption cross-section. Figure 4 is a SEM image of an

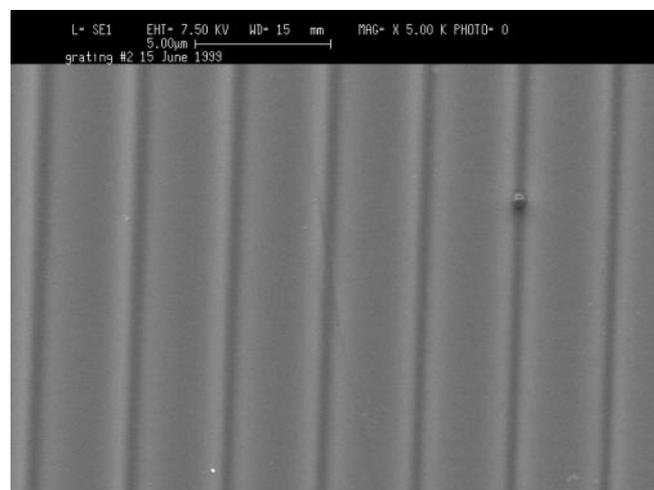


Fig. 4. SEM image of grating lines. Scale bar is $5 \mu\text{m}$

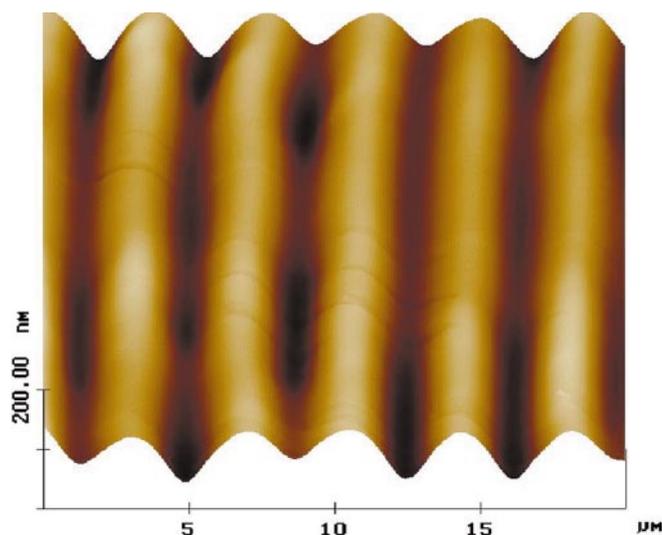


Fig. 5. AFM image of grating structure illustrating a $3.8\text{-}\mu\text{m}$ spacing and a 50-nm modulation depth

other grating written under the same conditions. The measured spacing from the image is about 3 μm . Figure 5 shows an AFM image of the grating region. The spacing was measured to be 3.8 μm with a modulation depth of 50 nm. Some variations in the grating profile can be observed. This is primarily due to pulse fluctuations over the time scale of the exposure. As the intensity pattern represents a statistical function of the probability of having a two-photon absorption event at a discrete molecular site, the exposure time should influence the filling factor of the polymerized region versus the unpolymerized region at a constant intensity. Subsequently, the diffraction efficiency should reflect this dependency. We define the diffraction efficiency, η , as the ratio of the energy in the first-order diffraction spot relative to the zeroth-order spot. Using a helium–neon laser as a reference wavelength, we find the following diffraction efficiencies versus exposure time. The diffraction efficiency values would imply saturation in grating efficiency as a function of time. From the diffraction pattern we also calculated a grating spacing of 3.5 μm .

The presented results demonstrate that using a dye with a very large two-absorption cross-section and a commercially available photopolymer, the process of two-photon-induced polymerization can be spatially controlled by using holographic techniques from a fs laser. This opens a path towards the rapid generation of three-dimensional microstructures for optical data storage and photonic band-gap materials as well as to the spatial 3D control of other photo-induced processes.

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