1-22-2018

Transport-of-intensity-based phase imaging to quantify the refractive index response of 3D direct-write lithography.

David J Glugla
Madeline B Chosy
Marvin D Alim
Amy C Sullivan
Robert R McLeod

Follow this and additional works at: https://scholar.colorado.edu/ecen_facpapers
Transport-of-intensity-based phase imaging to quantify the refractive index response of 3D direct-write lithography

DAVID J. GLUGLA,1,* MADELINE B. CHOSSY,2 MARVIN D. ALIM,3 AMY C. SULLIVAN,1 AND ROBERT R. MCLEOD1,3

1Department of Electrical, Computer, and Energy Engineering, University of Colorado Boulder, Boulder, CO 80309, USA
2Department of Chemistry, Carleton College, Northfield, MN 55057, USA
3Materials Science and Engineering Program, University of Colorado Boulder, Boulder, CO 80309, USA
*David.Glugla@colorado.edu

Abstract: Precise direct-write lithography of 3D waveguides or diffractive structures within the volume of a photosensitive material is hindered by the lack of metrology that can yield predictive models for the micron-scale refractive index profile in response to a range of exposure conditions. We apply the transport of intensity equation in conjunction with confocal reflection microscopy to capture the complete spatial frequency spectrum of isolated 10 μm-scale gradient-refractive index structures written by single-photon direct-write laser lithography. The model material, a high-performance two-component photopolymer, is found to be linear, integrating, and described by a single master dose response function. The sharp saturation of this function is used to demonstrate nearly binary, flat-topped waveguide profiles in response to a Gaussian focus.

OCIS codes: (120.0120) Instrumentation, measurement, and metrology; (160.0160) Materials; (220.0220) Optical design and fabrication.

References and links

Journal © 2018
Received 9 Oct 2017; revised 6 Jan 2018; accepted 9 Jan 2018; published 18 Jan 2018
https://doi.org/10.1364/OE.26.001851
4452, pp. 39–47.


1. Introduction

Direct laser writing (DLW) optical lithography is a common technique used to create micron-scale three-dimensional (3D) refractive index structures deeply buried within a photosensitive medium [1–3]. The primary applications of DLW have been 3D routed waveguides for interconnects to integrated optoelectronic circuits [3–7], 3D diffractive optics that provide greater control over the multidimensional coherence function than their 2D counterparts [8], and 3D optical data storage that extends the capacity of traditional surface recording [9,10]. Proper design for such applications demands the ability to understand this light/matter interaction, which includes characterizing the optical properties of both the focused writing beam and photosensitive material, and measuring the magnitude and shape of the resulting index response.

Inorganic photosensitive materials such as photorefractive crystals or photosensitive glass offer the ability to create non-volatile embedded refractive index structures through a post-processing thermal treatment, while offering reasonable one-photon sensitivity for DLW and holographic patterning [11–13]. Alternatively, the refractive index of most transparent amorphous or crystalline inorganic material can be modified at the focus of a sufficiently high intensity femtosecond pulse train [14,15]. However, the mechanism by which these structures
are formed is often complex \[16\] and inhibits the ability to accurately predict the shape and magnitude of the index response without performing extensive metrology. The lack of such predictive models limits the ability to design single-mode waveguides, control the scattering profile of volumetric diffractive optics, or predict the data storage density of an optical disk.

In contrast to their inorganic counterparts, organic materials such as polymers provide synthetic routes to a vast range of optical and mechanical properties. Typically, absorption of single or multiple photons by a photoinitiator molecule generates radicals or cations, which initiate monomer conversion to polymer. DLW lithography has been used to locally induce this monomer polymerization and form refractive index structures through the resulting material densification. However, formulations consisting of a single monomer species generally have minimal index response, as the initial localized polymerization is followed by a uniform bulk cure to render the material environmentally stable. To circumvent this issue, formulations typically mix high and low refractive index components whose fractional composition, and thus refractive index, is modified via mass transport when exposed to patterned illumination, but left nominally unchanged by the uniform post-processing cure \[17\]. The high photo-sensitivity of these two-component photopolymers, and their ease of processing, have led to applications in holography, 3D data storage, self-written waveguides \[18,19\], and laser direct-write lithography of waveguides \[7,20,21\]. Although the holographic community has invested significant effort both into developing a rational design for the material and understanding the index response to sinusoidal illumination \[22–26\], little has been done to quantitatively predict how these two-component photopolymer materials respond to a focused beam.

Thus, accurate measurements of the gradient index profile of both inorganic and organic photosensitive materials in response to single- or multi-photon absorption at a stationary or continuously moving laser focus is critical to enable a wide range of optical applications. This is an open problem fundamentally because quantitative metrology of weak (index contrast \(\sim 10^{-3}\)) and small (feature width \(\sim\)wavelength) buried 3D phase objects is a challenging task. In particular, all 3D optical metrology methods have a finite coherent transfer function (CTF) which will fail to accurately measure the peak or profile of the index response unless the object spatial frequency spectrum is completely within the instrument CTF. For example, Bragg diffraction from holograms written by two-beam interference and analyzed with Kogelnik’s coupled wave theory \[27\] only measures the first harmonic of the periodic illumination, losing information about the higher orders, and their contribution to the peak index. Digital holographic microscopy \[28,29\] and diffraction-based phase retrieval \[30,31\] have been applied to reconstruct buried waveguide profiles, however, in the case of perpendicular-write waveguides, the methods are constrained by poor overlap of the microscope CTF with the waveguide spatial frequency spectrum. Thus, further preparation of the sample, either via cross-sectioning, or the use of additional assumptions about the shape of the waveguide is required to measure the full index profile. Alternatively, a method similar to that of the ascending scan technique used to measure the relationship between the writing beam focus and the 3D voxel shape of solidified two-photon polymerized structures \[32\] can be used to improve the overlap of the CTF and the waveguide’s spatial frequency spectrum. The writing beam focus begins within the substrate, and a series of phase structures are created, shifting the focus upwards from the substrate by an amount \(\delta z\) between each structure. Because the substrate effectively truncates the focus spot in the z-dimension, measuring the differential optical path length (OPL) between each structure provides, thin, 2D slices that can be used to reconstruct the full 3D phase profile (see Appendix A). Since each differential 2D slice is considered uniform in depth, all spatial frequency content collapses onto the \(f_z = 0\) plane and falls within the CTF of a high NA microscope. Unfortunately for small voxels, the signal-to-noise ratio for the differential OPL between each z-shifted voxel is typically lower than the sensitivity of the phase imaging system, restricting the applicability of this scan to large, or strong phase structures. However, by using a thick, 2D phase slice to
study the material’s light-induced index response over a range of different exposure conditions, enough information could be gained to generate a predictive model for arbitrary exposure conditions.

As demonstrated in the following section, incomplete overlap between the object spatial frequency spectrum and the imaging system’s CTF prevents accurate reconstruction of many 3D refractive index structures such as embedded waveguides. Therefore, we propose to fully characterize the index response of photosensitive materials by creating refractive index structures in a geometry that guarantees CTF overlap. We then apply this predictive model to the design of structures such as buried waveguides, whose complete spectrum does not overlap with the CTF, and is not accessible outside the material. The problem of CTF overlap is solved by imaging a transverse slice of a waveguide with a high NA transmission microscope. Although techniques such as refractive near-field scanning [34] have been used to probe the entire 2D refractive index profile of waveguides using this geometry, they require point-by-point scanning over the entire waveguide face, which is inconveniently slow for the multi-parameter materials characterization scheme proposed here. Full field, intensity-based phase imaging schemes such as iterative phase retrieval [30], digital holographic microscopy [35], and the transport of intensity equation (TIE) [36] offer significantly faster and simpler measurements. Unfortunately, iterative phase retrieval is sensitive to support constraints and does not always guarantee convergence to a global solution, whereas digital holographic microscopy is subject to coherent noise artifacts. In contrast, TIE-based phase retrieval, developed by Teague [37], provides a direct and unique measurement of the transmitted phase, which is equal in the Born approximation to 2D integrated optical path length. However, to calculate refractive index from transmitted phase requires additional 3D information about the structure. For example, although previous work combined TIE-based phase imaging with diffraction tomography to estimate both the shape and refractive index of buried waveguides [36], the CTF of the imaging system used in this geometry was again insufficiently matched to the spatial frequency spectrum of the object, preventing a direct, quantitative measure of peak index or shape.

In this paper, we demonstrate rapid and complete quantitative characterization of isolated index structures written by direct-write lithography using a combination of TIE-based quantitative phase imaging and confocal reflection microscopy. By aligning the CTF of the transmission microscope with the spatial frequency spectrum of thin 2D test structures, we are able to measure the relevant spatial frequency response of the material and use this to unambiguously reconstruct the complete \( \Delta n \) profile without the need to perform tomographic measurements. The validity of this technique is demonstrated by fully characterizing the direct-write index response of a high performance holographic photopolymer. Counter to the predictions of radical photochemistry, the material is shown to behave linearly with intensity over a wide range of exposure intensities and times. Furthermore, the index response is found to fall on a single master curve, which provides a unique functional translation between integrated exposure dose and index response. We then show that this function can be used to predict the size and shape of written waveguides, including the nearly binary structures that can be created using the sharp saturation of the response function. This technique is experimentally simple and applicable to any photosensitive material with single- or multi-photon response, enabling the rational design and optimization of writing systems, materials, and 3D optical devices, including waveguides, volume computer generated holograms, and data storage systems.
2. Theory and Experimental Details

Overlap of the Object Spatial Frequency Spectrum and the Imaging CTF

Fig. 1. (a) Transmission microscope used to image the phase object. (b) Example of an ideal CTF for the transmission microscope configuration used in all of the following experiments, operating under coherent illumination with a 0.3 NA in a material with a refractive index of 1.5. (c-d) Measurement geometry for imaging perpendicular and parallel-write waveguides respectively. (e-f) 2D image of the normalized refractive index distribution seen by the instrument. The insets show the cross-sections along the respective lines. (g-h) Overlap of the object’s Fourier transform with the CTF (line) of the ideal imaging system from (b). The Fourier transform amplitude shown has been scaled by taking the square root and then normalizing the amplitude in order to show the structure more clearly. (i-j) The resulting reconstructed object using only the Fourier components that overlap with the CTF of the imaging system. The insets compare the ideal cross-sections seen by the microscope along the respective lines with the actual object cross-sections (black squares).
Figure 1 illustrates the impact of mismatch between the object spectrum and the CTF. Consider an ideal phase imaging system Fig. 1(a) operating in transmission. Independent of the specific imaging method, an instrument with a finite signal-to-noise ratio can only measure the fraction of the object spectrum within the CTF [Fig. 1(b)]. Now let this system be used to examine a buried waveguide written by moving the focus perpendicular [Fig. 1(c)] or parallel [Fig. 1(d)] to the axis of the focus. For purposes of illustration, the circularly-symmetric waveguide refractive index profile in both cases is chosen to be of similar shape as one demonstrated later in this paper. As shown in Fig. 1(g), the spatial frequency spectrum of the perpendicular-write waveguide poorly overlaps the CTF, particularly in the z-direction, independent of the microscope NA. An ideal reflection microscope has even worse overlap, particularly with structures written via laser direct-write lithography [33]. Conversely, the microscope CTF can effectively overlap the spectrum of a waveguide written by moving parallel to the axis of the focus [Fig. 1(h)] if the diffraction-limited spot size is smaller than the smallest written feature size. Crucially, the delta-function spectrum of a waveguide that is invariant in the z direction fits within the z-axis singularity of the transmission microscope CTF. Assuming an ideal reconstruction wherein the CTF is constant, the measured waveguide in the former case has little resemblance to the object, appearing to have a uniform cross section in z and a peak amplitude of only 15% of the actual structure. Conversely, the latter geometry perfectly reconstructs both the profile and the peak refractive index. Therefore, in order to accurately reconstruct the object, the CTF of the imaging system must fully overlap the spatial frequency spectrum of the object.

Two-Component Photopolymer Formulation

The two-component holographic photopolymer used in this paper is a gel consisting of a low refractive index, optically transparent, flexible matrix polymer swollen with a liquid photoreactive writing chemistry that consists of a photoinitiator and a high refractive index writing monomer [17]. Photons absorbed by the photoinitiator begin polymerization of the monomer, creating a local concentration of high refractive index polymer within the matrix. After re-equilibration of the unreacted monomer via diffusion, and the matrix via swelling, the resulting concentration variations of the low-refractive index matrix and high-refractive index polymer yield a difference in the refractive index ($\Delta n$), given by the volume-fraction weighted average of the constituent refractive indices [38]. A final uniform cure polymerizes all remaining monomer, preventing further mass transport, and resulting in minimal change to the bulk refractive index. Depending on the end-application, different chemical formulations have been developed to address the required material properties. Covestro and DuPont have both developed high dynamic range photopolymers with $\Delta n$’s ranging from >0.03 to 0.06 for the Bayfol HX and OmniDex formulations respectively [39,40]. These high $\Delta n$’s allow for the production of thin, volume holograms [41]. However, the high $\Delta n$ typically comes at the expense of increased shrinkage (1.4% for the Bayfol HX [39]), which is unsuitable for multiplexed holographic data storage. Using their DRED formulation, Akonia Holographics has demonstrated a low-shrinkage version of a two-component photopolymer (<0.1%) for holographic data storage with a zero-to-peak $\Delta n$ as high as 0.015 [42]. Although predictive models have been developed to describe the formation of periodic holographic phase structures within such materials [43], to the best of our knowledge, little work has been done to model the material response when writing isolated phase structures such as waveguides.

The writing monomer used in the model two-component photopolymer is phosphorothioyltris(oxybenzene-4,1-diylcarbamoyloxyethane-2,1-diyl) triacrylate, and was synthesized following a procedure reported in various Covestro patent literature [44]. First, 0.0207g (0.09 mmol) of 2,6-di-tert-butyl-4-methylphenol and 57 mL of Desmodur RFE (27% solution of tris(p-isocyanatophenyl) thiophosphate in ethyl acetate, 38.9 mmol) were added to a dried 100 mL round bottom flask with a magnetic stir bar. The reaction was started by
adding 13.5 g (116.3 mmol) of 2-hydroxyethyl acrylate to the flask dropwise, and was performed at 60°C with a reflux condenser overnight. The product was collected by cooling and subsequent removal of ethyl acetate in vacuum to obtain a waxy semicrystalline solid. In order to form the photoreactive component of the photopolymer, a 1:10 molar ratio of photoinitiator TPO (2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide) to the writing monomer was used.

The crosslinked matrix of the two-component photopolymer system is a flexible polyurethane with a glass transition temperature \( T_g \) of \(-45^\circ\text{C}\), and consists of a 1:1 molar ratio of isocyanate (Desmodur N3900) and alcohol (polycaprolactone-block-polytetrahydrofuran-block-polycaprolactone). In the following experiments, formulations with overall weight fractions of 10% and 30% of the photoreactive components were used. Test samples were fabricated by mixing the matrix and photoreactive components at 60°C, prior to gelation of the polyurethane, degassing the resin, and then casting between a 1 mm glass microscope slide and a 150 \( \mu\text{m} \) glass coverslip. Sample thickness was set using spacers ranging between 13 and 25 \( \mu\text{m} \). Polymerization of the urethane matrix occurred overnight in an oven at 60°C.

**Exposure and Confocal Reflection System**

The optical layout shown in Fig. 2 is used to fabricate the sample phase elements for TIE-based imaging and analysis. The sample is mounted on a 5-axis stage that controls both tip/tilt and xyz motion, while a confocal reflection microscope operating at 660 nm is used to align the sample and provide a non-contact method for precisely measuring the thickness of the sandwiched photopolymer layer. The confocal beam is co-aligned with a second laser at 405 nm central wavelength that is used to expose the photopolymer. Because the chosen photoinitiator is minimally absorptive at 660 nm, the confocal imaging system will not initiate significant polymerization and can therefore make optical path length measurements at the direct site of the exposure. The known refractive index of the photopolymer at this wavelength, measured with a Metricon Model 2010 prism coupler, is used with the optical path length measurement to calculate the thickness of the sample. When performing quantitative phase imaging of a 2D profile, this thickness measurement is necessary for determining the actual \( \Delta n \) from the measured optical path length. A 0.66 NA objective is used in conjunction with a 10 \( \mu\text{m} \) pinhole to give a confocal axial resolution of \(~2 \mu\text{m}\) within the material [45] and a thickness uncertainty of \( \pm 2.5\% \).

At each location, the thickness of the sample is measured by the procedure above, then the 405 nm light beam exposes a series of 2D, isolated gradient index structures into the material using a range of intensities and exposure times. The small size of the structures and high stiffness of the glass coverslip relative to the rubbery polymer are presumed to prevent change of thickness due to polymerization shrinkage or swelling of the matrix. Before exposure, the 0.66 NA objective is replaced with a 0.13 NA, 4× Nikon objective operating at an effective NA of 0.023 to provide a focused spot 1/exp(2) intensity diameter of \(~18 \mu\text{m}\). The total beam power is controlled using both the driving current and a variable ND filter in order to achieve a large range of intensities. Exposure time is controlled using a Uniblitz VS14 shutter with a minimum equivalent exposure time of 4.5 ms. Three points are written for each exposure condition to provide error bars.
Fig. 2. The confocal reflection microscope (660 nm path) is used to position and measure the sample thickness, while the co-aligned 405 nm laser is used to expose the photopolymer and create phase structures (inset shows an example differential interference phase contrast microscopy image). The 660 nm laser is a 100 mW Coherent OBIS LX diode laser, and the 405 nm laser is a Power Technology Incorporated IQ2A105/8983 105 mW laser.

**Phase Imaging**

The refractive index contrast between the written phase structures and the base matrix is measured using a non-interferometric phase imaging technique based on the solution of the transport of intensity (TIE) equation

\[
2\pi \frac{\partial I(r, z)}{\lambda_0} = \nabla_{\perp} \left[ I(r, z) \nabla_{\perp} \Phi(r, z) \right]
\]

where \( I(r, z = 0) \) is the in-focus image intensity distribution perpendicular to the optical axis \( \hat{z} \), and \( \lambda_0 \) is the wavelength of the incident light (vacuum). The optical path length along the optical axis is \( \Phi = k_0 n L \), where \( k_0 = \frac{2\pi}{\lambda_0} \), \( n \) is the refractive index of the material, and \( L \) is the thickness of the structure. In order to solve the TIE, a series of Fourier transforms \( \mathcal{F} \) are applied as shown in Eq. (2) and (3) [46,47]:

\[
\Phi(r, z) = \mathcal{F}^{-1} \left[ \frac{\mathcal{F}(\nabla_{\perp} I^{-1}(r, z) \nabla_{\perp} \Psi(r, z))}{4\pi^2 (f_x^2 + f_y^2)} \right]
\]

and \( f_x, f_y \) are the spatial frequency components of the image. Aside from the wavelength of light, only knowledge of the axial intensity derivative is required. Because the axial intensity derivative can be estimated with a series of defocused images, and the TIE does not suffer from strict coherence requirements of the illumination source, this technique offers a simple method for direct phase measurements [48,49]. In the following experiments, imaging to determine the axial intensity derivative is performed with a conventional brightfield microscope equipped with a 633 nm line filter, a 20×, 0.5 NA objective, and a condenser operating at 0.3 NA to broaden the linear spatial frequency response range of the TIE [50]. The axial derivative is approximated via a second-order central difference approximation.
using a pair of symmetrically defocused images about the in-focus image plane. The detector noise in this approximation sets a limit on the minimum defocus distance, while the error associated with the second-order finite difference approximation imposes a competing limit on the maximum defocus distance [51,52]. Although a variety of techniques exist to reduce this noise, most commonly by acquiring larger sets of defocused images, a single pair is found to be sufficient [53–55]. A defocus distance of ±3 μm around the object plane using a piezo actuator provides the best experimental results for the given setup (see Appendix B). Additionally, because fast Fourier transforms are used to solve the TIE, periodic boundary conditions are assumed. While the addition of an aperture at the image plane can be used to bypass this assumption [56], the imaged phase structures in the following experiments are sufficiently isolated that the phase difference falls to 0 at all of the boundaries, thereby satisfying the required boundary condition. Finally, because the depth of field of the writing illumination is significantly larger than the thickness of the sample, and the absorption of the sample is insignificant over these thicknesses, the index of refraction of the written phase elements is uniform throughout the thickness of the sample. In other words, we measure here the response of the polymer to a stationary focus. One could also translate the focus through the thin sample of photosensitive material to simulate the continuous translation of a waveguide writing experiment. In either case, the index distribution is invariant in the axial direction and the object spatial frequency distribution is thus confined to the plane $f_z = 0$.

This guarantees no loss of information outside of the transmission microscope CTF as long as the NA of the objective used for TIE is much greater than that used for writing (Fig. 1.).

With this geometry, the only 3D knowledge required to translate the phase measurement to the complete 3D refractive index profile is the precise thickness of the sample, which is provided by the integrated confocal reflection microscope. An example of the calculated refractive index structure for a Gaussian exposure is shown in Fig. 3. Verification of the TIE algorithm was performed by comparing the measured height profile of a microlens array using both the TIE algorithm and atomic force microscopy (see Appendix C).

Fig. 3. (a-c) Example brightfield images required for solving the TIE, including two symmetrically defocused images (a,c) and one in-focus image (b). (d) The 2D reconstructed $\Delta n$ using the images from (a-c) along with representative (e) cross-sections taken along the x- and y-axes.
3. Results and Discussion

Single Exposure Material Response

In order to completely quantify the $\Delta n$ response of the two-component photopolymer, a series of isolated, Gaussian-shaped photoexposures are applied to the material using the 405 nm wavelength excitation source. Varying the exposure time and writing intensity provides control over the $\Delta n$ modulation, which is measured using confocal reflection microscopy and the TIE as discussed above. The concentration of writing monomer within the material is also varied between 10 and 30 wt% to measure the effect of the formulation on the $\Delta n$ response to exposure. While the method measures the complete index profile, Fig. 4 shows just the index at the peak of each exposure as a function of time, intensity and formulation.

The figure illustrates how a very large number of exposure conditions and material formulations can be rapidly evaluated, enabling a complete material characterization. For the model material, the measured data [Figs. 4(b) and 4(c)] reveal an inhibition period at low exposure times and intensities, consistent with the initial consumption of oxygen by the radical initiating species [57,58]. After this induction period, the materials respond monotonically with exposure time, exhibiting greater slope for higher intensity and monomer concentration. At large exposure times and intensities, the index response saturates. The saturation $\Delta n$ of the 10 wt% monomer formulation of $7 \times 10^{-3}$ is half that of the 30 wt% monomer formulation at $1.4 \times 10^{-2}$, indicating the material sensitivity and maximum obtainable $\Delta n$ are limited by the initial monomer concentration. To support this hypothesis, photoinitiator consumption has been calculated to be negligible over the given exposure times and intensities (see Appendix D).

Finally, the panels in Figs. 4(d) and 4(e) show that the raw data can be collapsed to a single master curve for both materials in which index response depends only on the product of intensity and exposure time. One possible explanation for the deviation from this fit at low intensity exposures in the 10 wt% monomer loading is the in-diffusion of new inhibiting oxygen species. However, in the general case, this linear, reciprocal behavior is contrary to the expected behavior of neat acrylate monomers and radical initiators, which should exhibit sublinear (typically square root) intensity dependence due to bimolecular termination. Although some bulk and holographic characterization of such polymers has found reciprocal behavior [22,59], common models based on pseudo steady-state analysis and bimolecular termination assume a sub-linear behavior [60]. Such sub-linear behavior dramatically limits confinement of structures written by a focused beam [61], while conversely, the completely linear behavior shown here drastically simplifies the design of complex 3D index structures.
Fig. 4. (a) Differential interference contrast microscopy image of a subset of the measured phase structures. (b-e) The peak $\Delta n$ response for the model two-component photopolymer over a range of different exposure intensities, exposure times, and monomer loadings as measured by TIE-based quantitative phase imaging in conjunction with confocal reflection microscopy. (b) The $\Delta n$ vs. exposure time for 10 wt% monomer loading. (c) The $\Delta n$ vs. exposure time for 30 wt% monomer loading. (d) The $\Delta n$ vs. exposure dose for 10 wt% writing monomer. (e) The $\Delta n$ vs. exposure dose for 30 wt% writing monomer. Each symbol corresponds to 3 isolated exposures, each of which has been measured by the method described in the text. Error bars show the total spread of the three measurements.

The linear, integrating response of the material is further demonstrated in Fig. 5, where a series of phase structures was created with the focused 405 nm Gaussian beam for various exposure times. For each structure, the first exposure was immediately followed by three additional exposures of the same duration and intensity. The TIE/confocal reflection measurement was used to measure the resulting $\Delta n$ profile, shown in Fig. 5(a). As shown in Fig. 5(c), the material responds only to total dose, again falling on a single master curve. The
shape of the structure, characterized in Figs. 5(b) and 5(d) through the full width at half maximum (FWHM), also depends only on the total exposure dose and is invariant to the total number of exposures. These results demonstrate that the material integrates optical exposure dose with no hysteresis such that a designer can fabricate overlapping phase structures without considering the order in which they are exposed. This behavior is expected to hold as long as subsequent exposures occur before significant diffusion of the writing monomer occurs.

Fig. 5. (a-b) The $\Delta n$ response and FWHM for a series of phase structures that are exposed up to 4 times immediately after the initial exposure. For low doses below the saturation limit, the $\Delta n$ continues to increase until the final saturation $\Delta n$ is reached. Continued growth of the structure terminates due to consumption of all local monomer. (c-d) The $\Delta n$ response and FWHM for the same structures plotted against the total exposure dose.

**Predicting Phase Structure Profile with the Material Response Master Curve**

The previous sections demonstrated TIE phase recovery and confocal reflection microscopy of laser direct-write lithography samples oriented such that the object spatial frequency spectrum was fully within the microscope CTF. This enables quantitative, rapid, and complete characterization of photosensitive material response to intensity, exposure time, material formulation, and multiple exposures. For the model material used here, which is linear and integrating, the peak index response $\Delta n$ was shown to fall on a single master curve as a function of total dose. While particularly convenient, multivariable response models could be developed for other materials using the methods presented.

Since the complete spatial frequency spectrum of buried waveguides cannot be accessed by any instrument that is outside the material, we suggest that the appropriate design flow for laser direct-write lithography of 3D phase structures is to first generate the material response
model as shown above. Then, the model can be applied to predict the material index response to known exposure conditions that are used to write buried structures whose profile cannot be directly measured. To show that such an approach is valid, here we apply this technique to predict the size and shape of waveguide profiles written in the end-face geometry used above, such that the prediction can be compared to a quantitative measurement.

Here we use the material with 30 wt% monomer loading because of its larger saturation index and single response curve for all exposure conditions. This reference curve, is extracted from the peak index response data in Fig. 4(e), smoothed using a Gaussian filter, and then interpolated using the piecewise cubic hermite interpolating polynomial (PCHIP) method in MATLAB [Fig. 6(a)]. Given an arbitrary exposure profile and peak intensity, the curve predicts the amplitude and shape of the resulting phase element without the need for additional tomographic reconstruction of the individual structure. To demonstrate this, a series of 2D Gaussian exposures was performed in the photopolymer loaded with 30 wt% writing monomer, and the predicted transverse index profiles of the structures were compared to the measured $\Delta n$ profile using TIE/confocal reflection microscopy [Figs. 6(b)–6(d)]. Both the peak $\Delta n$ and FWHM predictions agree with the measured values over doses spanning 25 to 570 mJ/cm². At small doses, the predicted FWHM deviates, in part due to the low signal-to-noise ratio associated with the TIE for weak phase elements.

The proposed method accurately predicts the complete profile of the waveguide, even far into the saturation regime of the material. Specifically, the relatively sharp transition between the proportional and saturated dose response of the model material enables the formation of nearly binary channel waveguides that would support tightly confined modes, as shown in Fig. 6(b). This in turn would enable the use of beam shaping methods originally suggested for femtosecond lithography of glasses with nearly binary response [62]. Design of such buried, shaped structures in response to shaped foci or multiple-passes is made possible by the characterization method described here.
4. Conclusion

By ensuring overlap between the CTF of the imaging system and the written phase structure, we have demonstrated the ability to completely characterize the refractive index change resulting from a DLW exposure within a two-component photopolymer. Using this information about the material response, we were then able to predict both the resulting amplitude and shape of the refractive index perturbation that developed in response to an arbitrary exposure dose profile. This technique overcomes the limitations and experimental difficulty of conventional tomography and enables the ability to design and fabricate known 3D phase structures within a photosensitive material. Although the demonstration was performed in a two-component photopolymer, this technique is applicable for any transparent, photosensitive material that produces a localized change in the refractive index, proving useful for both evaluating the phase response, and fabricating isolated waveguide structures in a variety of photosensitive materials.

Appendix A: Ascending Scan Technique

The ascending scan uses the substrate to truncate the exposed 3D phase voxel. By moving the focus away from the substrate by an amount $\Delta z$ between each exposure, and measuring the differential path length between adjacent structures, the full 3D profile of the voxel can be measured (Fig. 7). Because each differential phase slice is considered uniform over the distance $\Delta z$, the Fourier transform collapses to a single dimension and can fall within the CTF of a microscope imaging system.
Fig. 7. The shape of 3D phase structures written into a material using either two-photon polymerization or a thresholded single-photon polymerization response can be measured using the ascending scan method. The focus of the exposure beam is shifted by an amount $\Delta z$ between each exposure until the substrate no longer truncates the resulting phase structure. Phase imaging can then be used to measure the differential optical path length between adjacent structures. Because these thin phase slices are assumed to be uniform in $z$, the spatial frequency content of each slice falls entirely within the CTF of the imaging system. Therefore, measuring each of the differential slices in the 3D structure allows one to reconstruct the entire voxel.

Appendix B: Optimal Defocus Distance for the Transport of Intensity Equation

The optimal defocus distance that minimizes the noise from both the axial intensity derivative approximation and that associated with the nonlinear error from the TIE approximation occurs at the distance where the peak $\Delta n$ begins to decrease. For the phase structures fabricated in the experiments, it is $\sim 3 \, \mu m$ (see Fig. 8).

Appendix C: Verification of the TIE Algorithm

The topography of a fused silica microlens array (Suss MicroOptics) with circular lenses was characterized using both the TIE algorithm and atomic force microscopy (AFM) as seen in Fig. 9. The quoted radius of curvature (ROC) for the microlenses is $42 \, \mu m$ with a pitch of 30
μm. The ROC measured using the TIE was 41 μm while the ROC obtained using AFM was 43 μm. The height of the lenses agreed within 100 nm for the two different measurement techniques.

![Fig. 9. (a) Brightfield microscope image showing the region of the microlens array used to test the TIE algorithm. (b) Reconstructed thickness profile of the boxed region in (a). The blue line shows the cross-section used in (c). (c) Cross section of a single microlens obtained through the TIE algorithm and atomic force microscopy. The radius of curvature agrees with the manufacturer quoted value of 42 μm.](image)

Appendix D: Photoinitiator Depletion

The photoinitiator concentration vs exposure time at a number of different intensities has been plotted and overlaid with the exposure time required to achieve Δn saturation (Fig. 10). The plot shows that photoinitiator is not significantly consumed before saturation of the Δn. Therefore, finite monomer concentration limits the total achievable Δn for a single exposure.
Fig. 10. Plot showing the photoinitiator concentration vs. exposure time for different exposure intensities. The time required to reach saturation of $\Delta n$ is plotted as circles. Saturation is reached well before a significant fraction of photoinitiator is consumed.

**Funding**

National Science Foundation (NSF) (EFRI-1240374, 1721055, 1307918).

**Acknowledgments**

Portions of this work were presented at SPIE Optics + Optoelectronics (Holography: Advances and Modern Trends V) in 2017, Analysis of holographic photopolymers for integrated optical systems via quantitative phase microscopy; doi: 10.1117/12.2265873.