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Liquid Deposition Photolithography for the fabrication of gradient index (GRIN) micro-optics

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ABSTRACT

One photon diffusive photopolymers enable self-developing three dimensional (3D) refractive index patterning of up to cm thick solid volumes for the fabrication of micro-optics. However, one photon absorption in solid, thick materials does not yield complete control of the 3D refractive index distribution due to diffraction and the excessive development time for index features measuring 100's of microns in diameter or larger. We present a fabrication method and photopolymer formulation that can efficiently create mm^3 optical devices with programmable, gradient index of refraction with arbitrary feature size and shape. Index contrast of 0.1 is demonstrated, which is 20 times larger than commercial holographic photopolymers. Devices are fabricated by repetitive micro-fluidic layering of a self-developing photopolymer structured by projection lithography. The process has the unusual property that total fabrication time for a fixed thickness decreases as the number of layers is increased, reducing the fabrication time for high axial resolution micro-optics. We demonstrate the process by fabricating thick waveguide arrays and gradient index lenses.

1. Introduction

One photon diffusive photopolymers [1-3] enable self-developing 3D patterning of up to cm thick solid volumes for the fabrication of optical devices. The low required dose ($\sim 100 \text{ mJ/cm}^2$) and wavelength sensitivity (UV to near IR) of these materials have led to applications in optical data storage [4] with 1.6 TB capacity and 960 Mbit/s data rates, and photonic devices such as waveguides [5], holographic filters [6], and GRIN lenses [7]. However, one photon absorption in solid, thick materials does not yield complete control of the 3D index distribution due to diffraction. Additionally, the required diffusion time for development of structures of size

L scales as L^2/D where diffusivity D is typically $\sim 1 \mu\text{m}^2/\text{s}$, limiting maximum feature size to 100's of microns.

Multi-photon absorption can be utilized to restrict out-of-focus response and obtain more complete control of the 3D index distribution. Unfortunately, multi-photon absorption requires femtosecond pulse length for efficient excitation. Glass is the most common base material due to its high environmental stability, but requires irradiances of 10^{17} W/m^2 or larger and device thickness is restricted to the working distance of an oil-immersion objective. Most applications are sparse waveguide devices [8-11], though dense 3D index patterns such as volume computer generated holograms (VCGH) [12] have been generated, but only contain 64^3 features. To increase throughput and eliminate depth restrictions, liquid polymers [13] containing photo-initiators with large two-photon cross-sections and polymerization chain-reactions to increase sensitivity are used. Sparse waveguide [14,15] devices have been fabricated and scanning point exposures have created dense 3D structures including invisibility cloaks [16] and templates for a gold polarizer [17]. However, the fabrication rate for the polymer structure of the invisibility cloak described in reference 16 is 13 years/ mm^3 , because the necessary power density still requires rastering through a large number of very small voxels, generally limiting devices to sparse, typically binary structures with small voxel count.

Here we show a fabrication process, liquid deposition photolithography (LDP) and an initially-liquid photopolymer to fabricate optical components containing sub-micron resolution 3D index structures. The fabricated optical components can have an index contrast up to 0.1, allowing greater flexibility in device fabrication. High throughput is enabled by using an initially-liquid photopolymer, which enables micro-fluidic manipulation and rapid monomer diffusion. The 3D volume is created through repetitive layering, where each layer is structured by projection lithography. With this process and material we demonstrate passive optical component fabrication.

2. Liquid Deposition Photolithography

2.1 Process Steps

The process steps for LDP are shown in Figure 1. Layers are created by drawing liquid monomer through a microfluidic gap between the chamber window and platform created as the platform is lowered. The layer thickness is controlled by the distance the platform is lowered, enabling sub-micron precision of layer thickness. Two dimensional (2D) projection lithography through the chamber window structures the index of each layer and the process repeats. The chamber window provides optical access and prevents stiction by maintaining a thin liquid layer at the top of the polymer, allowing many layers to be written.

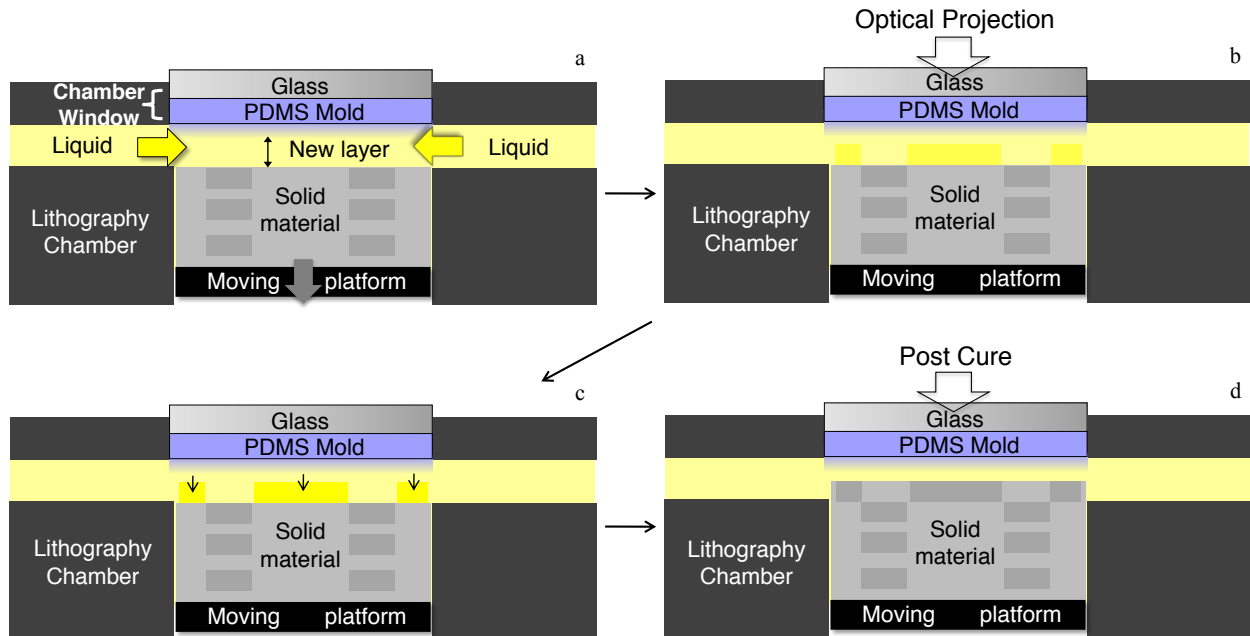


Figure 1: Steps of Liquid Deposition Photolithography (LDP) process. a) UV sensitive liquid monomer is drawn through a microfluidic channel created as the platform is lowered, producing a new layer. b) The new liquid layer is patterned by 2D projection lithography, using 365 nm light, polymerizing the liquid monomer into a solidified gel of the 2D pattern. Polymerization is suppressed just below the window via inhibitor diffusion from the polydimethylsiloxane (PDMS) mold. c) Unreacted monomer diffuses from this adjacent layer of liquid monomer into the solid to replace that consumed by polymerization. This diffusion increases the material density and index of refraction in the exposed region. d) The entire layer is optically flood cured, using 365 nm light, to a solid, cross-linked, photo-insensitive polymer. Steps a through d are repeated to fabricate complex 3D index structures.

Processing time in LDP is reduced compared to conventional lithography because the entire process is completed on a single instrument. Therefore, the separate instruments for each step of the process are not required, including the mask-to-substrate alignment, layer planarization, and chemical and thermal processing. Thermal and wet processing steps can be eliminated because the material used is a self-developing diffusive photopolymer that does not require additional processing to develop, which is not the case for the resists used in conventional lithography. Similar to conventional lithography, transverse resolution is a function of the projection optics, material response and layer thickness, while axial resolution is determined by layer thickness. In LDP, the layer is not spin coated but deposited by the motion of a stage and planarized by the chamber window. This enables many micrometer thick layers to be sequentially fabricated.

2.2 The chamber window

The chamber window is critical to the LDP process because it prevents polymer adhesion to the window and it enables each thin layer to be structured by aberration-free projection lithography. The chamber window, a 125 μm thick polydimethylsiloxane (PDMS) layer

that is adhered to cover glass, was originally developed to allow optical pattern access and prevent polymer adhesion to the window for efficient fabrication of micron sized particles [18]. We have extended the use to passively planarize new layers as a mold and maintain a monomer-rich liquid layer next to the exposed part. The chamber window performs these functions by providing a constant flux of oxygen at the liquid monomer boundary via diffusion from the PDMS layer. Oxygen is a strong radical inhibitor [19], so polymerization is prevented in the thin liquid monomer layer directly adjacent to the chamber window. Oxygen is used as the inhibitor because it is naturally present via atmospheric diffusion, is a well-characterized inhibitor of radical polymerization and diffuses rapidly due to its small size. Details of the inhibition process are revealed in a reaction/diffusion simulation shown in Figure 2a. The simulation shows that the oxygen is consumed by photo-generated radicals at all depths, except near the window where it is continually replenished via diffusion from the PDMS. This inhibits conversion in a one-micron layer, preventing adhesion of polymer to the window and providing a high-concentration monomer source for subsequent diffusional mass transport into the exposed layer.

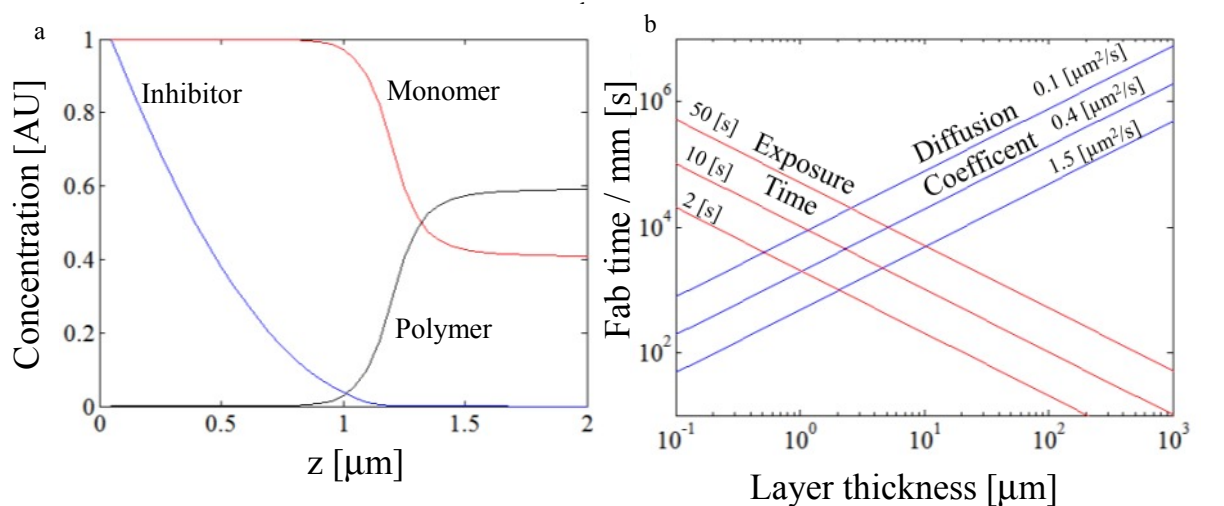


Figure 2: Reaction/Diffusion simulations of LDP. a) Concentration of inhibitor, monomer, and polymer immediately after completion of exposure. b) Total time required to complete exposure and diffusion of a one mm total-thickness part as a function of the individual layer thickness for various per layer exposure times and diffusion coefficients for materials similar to the material used for the experiments shown here. Depending on both the exposure time and monomer diffusion constant, there is an optimal layer thickness on the order of one micron that minimizes total fabrication time,

The time to fabricate a single layer consists of the pattern creation time set by the SLM frame rate, exposure duration and monomer diffusion time. SLM rates are typically negligible and exposure times, which are independent of layer thickness, are on the order of 10 seconds, which can be varied by material sensitivity ($\sim 100 \text{ mJ}/\text{cm}^2$) and pattern intensity ($\sim 10 \text{ mW}/\text{cm}^2$). In-diffusion of monomer that creates the index structures is from the liquid layer into the gelled solid, which therefore scales like layer thickness squared. This short diffusion length enables rapid fabrication of thick, high axial resolution optical components independent of the final scale of the index structure. For a fixed part thickness T , total diffusion time for all layers of thickness L scales like $(T/L)(L^2/D) = T L / D$ and thus decreases linearly with layer thickness, as shown in Fig. 2b. The relationship between axial resolution and fabrication time is therefore unusual, in

that higher resolution result in faster write times. This relation breaks down for sufficiently thin layers where exposure duration time dominates.

3. Liquid Diffusive Photopolymer

Index structure formation in diffusive photopolymers is still an active area of research [20, 21], however the understood mechanism is that index structures are formed by a spatially controlled increase in the density of a high refractive index monomer. The increase in the density is created when structured optical excitation of the photoinitiator initiates polymerization of the monomer in the illuminated regions. This locally depletes monomer in the exposed region, creating a concentration gradient of unreacted monomer between the illuminated and the dark regions. The concentration gradient causes diffusional mass transport of unreacted monomer from the dark regions to the exposed regions. This results in an increased monomer density and index of refraction in the exposed areas.

To enable the process of monomer diffusion, a solid matrix material is required to provide a physical scaffold to support and stabilize the structure. In one-component photopolymers, this scaffold is formed by incomplete polymerization of a single monomer. Photopolymerization and diffusion of the remaining monomer creates the index pattern, however, this results in low index contrast. To increase index contrast, two component photopolymers are formulated from both a low-index and a high-index monomer. The low index monomer is thermoset to form the solid scaffold while the high index monomer is photo-initiated to drive diffusional mass transport. However, the thermoset matrix cannot be sequentially layered, which is required for the LDP process, so traditional two-component photopolymers cannot be used. Therefore, a two-component mixture, in which both the low-index matrix and high-index diffusing monomer are liquid photopolymers was developed as shown in Figure 3.

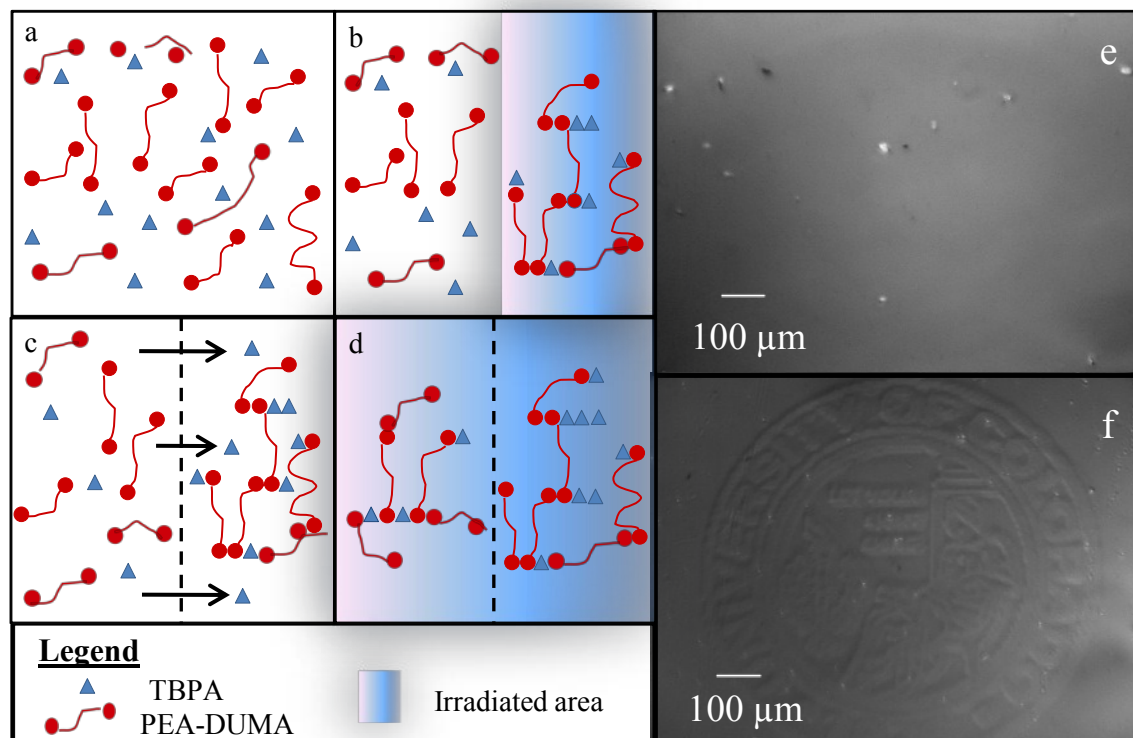


Figure 3: The material formulation contains two photopolymerizable monomers with different refractive indices and molecular weights. The low index, high molecular weight monomer, poly(ethylene glycol)-di(urethane methacrylate) (PEA-DUMA), is represented by two red circles connected by a line indicating its two functional groups. The high index, low molecular weight tribromo-phenyl acrylate (TBPA) is represented by a single blue triangle indicating its single functional group. a) The mixture of photoinitiator and monomers are injected into the exposure region in the form of a thin liquid layer. b) A portion of the area is exposed which locally consumes both monomers creating a low-index solid. c) Due to its smaller molecular weight, TBPA preferentially diffuses in to replace that consumed by polymerization, increasing the index of the exposed region. Note that in the LDP system, the majority of this diffusion is out of the inhibited layer through the thin depth of the part, not transversely across the large part width. d) After the mass transport of TBPA has concluded, the entire layer is exposed, polymerizing the remaining monomer to create a solid, cross-linked, insensitive polymer with approximately uniform PEA-DUMA and photo-patterned TBPA. e) In this control experiment, the TBPA was not present. The phase micrograph of the 3 μm thick structure shows no measurable index change. f) Phase micrograph of a 3 μm thick index structure with the same exposure conditions as (e), but containing TBPA

Rapid polymerization of the methacrylate matrix is followed by diffusion and then polymerization of the slower acrylate monomer. This formulation can be injected and photo-cured into thin layers like a one-component photopolymer but achieves the high-index contrast typical of two-component photopolymers. To demonstrate the efficacy of this material design, a material without high-index monomer develops very low index contrast as shown in Fig. 3e, but

a material with high-index monomer under the same exposure conditions exhibits much stronger contrast, as shown in Fig. 3f.

4. Parallel waveguide array fabrication

Waveguide arrays have many applications in photonics including high-bandwidth, multi-channel data links and endoscopic image transmission. Established methods for 2D waveguide array fabrication include the stack-and-draw technique for optical fiber arrays, multilayer planar lithography, and direct-write lithography in glasses and polymers. While these methods each have advantages and disadvantages for producing waveguide arrays for specific applications, each encounters problems with cost, complexity, and/or fabrication time when attempting to scale to large channel counts. In this section, we demonstrate liquid deposition photolithography (LDP) as a platform for 2D waveguide array fabrication with large channel counts.

A one-mm-thick rectangular waveguide array containing over 5,000 waveguide arrays was fabricated. To fabricate the rectangular waveguide array, 100 layers measuring $12\ \mu\text{m}$ thick were sequentially exposed with a 2D array of optical spots, structuring the index of each layer as shown in the cross-section shown in Figure 4(a). The fabricated waveguide array was tested by illuminating the front facet with a plane wave and imaging the end facet onto a CMOS camera, shown in Figure 4(b). The index contrast of the waveguide array, measured via scanning optical microscope, was measured to be 0.1, as shown in Figure 4(c). Array pitches ranging from 30 to 200 μm have been produced by changing projected optical pattern. The fabrication rate for the completion of the waveguide array shown was 1.2 hours per mm^3 .

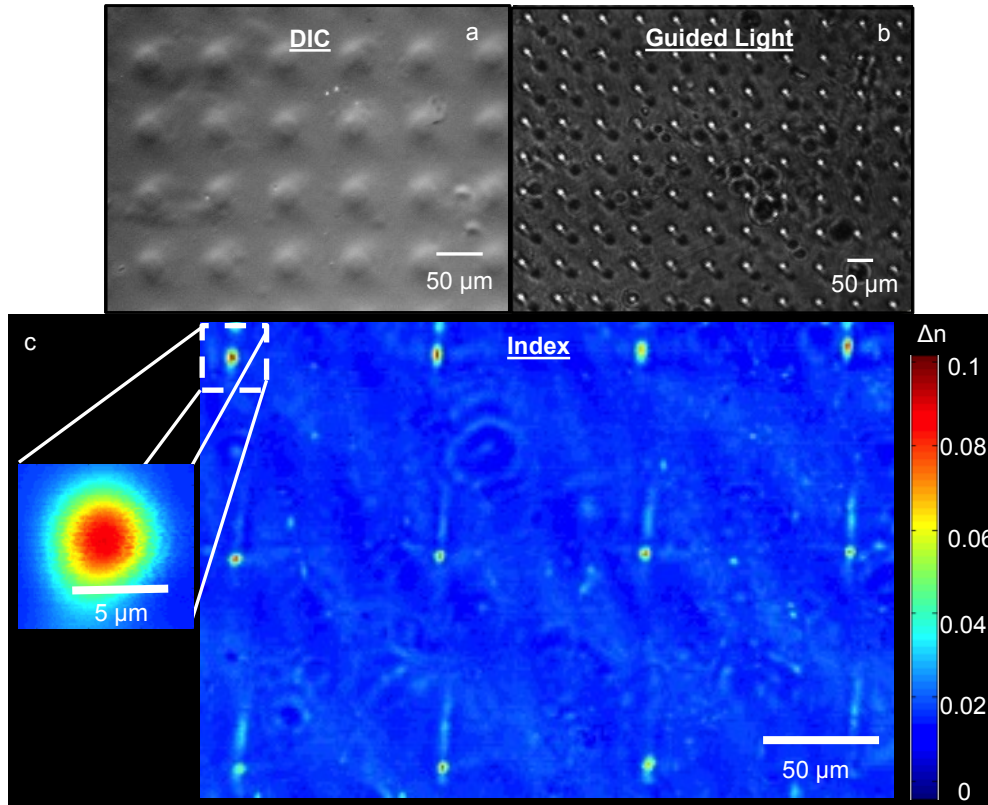


Figure 4. Parallel waveguide array fabrication. (a) DIC micrograph of a $80\ \mu\text{m}$ pitch rectangular waveguide array pattern written in a single $10\ \mu\text{m}$ layer. (b) Image of the end facet of $80\ \mu\text{m}$ pitch rectangular waveguide array, fabricated by sequentially-writing 100, $10\ \mu\text{m}$ thick layers, where the front facet was illuminated with a plane wave at $633\ \text{nm}$. (c) Refractive index map of the end facet of the rectangular waveguide array shown in (a-b).

LDP has the ability to be scaled to large channel counts with minimal impact on cost, complexity, or fabrication time. The channel count is limited by the number of resolvable spots of the optical system and the physical size of the lithographic chamber, making large channel counts possible by projecting a large number of resolvable spots and/or incorporating a step and repeat capability into the exposure process. Additionally, the fabrication time is equivalent for small and large channel count arrays due to the short longitudinal diffusion path created by the PDMS window, making LDP an attractive platform for large channel count waveguide arrays.

5. GRIN lens fabrication

Gradient index (GRIN) lenses have a wide range of applications including fiber optic communication, imaging systems, and medical devices. However, current GRIN lens fabrication methods, such as ion exchange [23] and chemical vapor deposition [24], are limited to a small set of 2D GRIN profiles which can be fabricated. To overcome this limitation, we demonstrate a

new method of GRIN lens fabrication that can print complex 3D GRIN parts with a large degree of control over the lens parameters.

To spatially modulate the intensity distribution and index distribution of each layer, a deformable mirror device (DMD) is used as the lithographic mask, as shown in Figure 5. With this system we can fabricate GRIN lenses with controllable 3D index profiles by changing the layer thickness and the intensity distribution of each projected pattern.

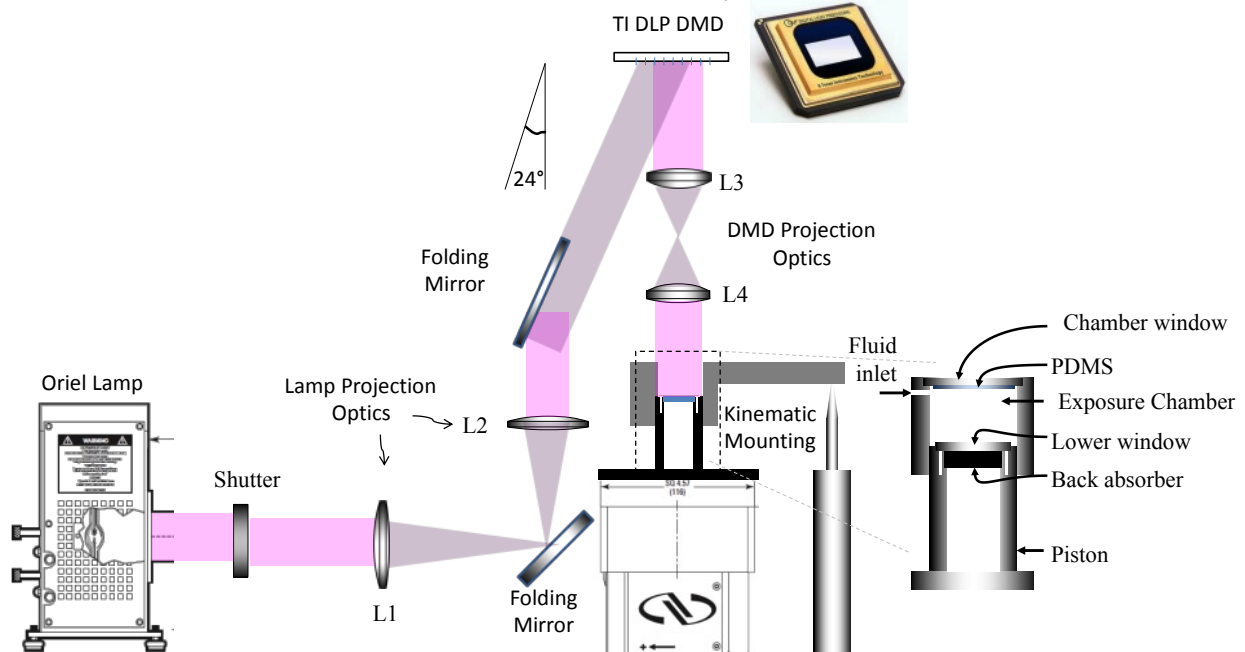


Figure 5. Optical setup of LDP for gradient index lens fabrication. Light is relayed from the output of the Oriol lamp to the DMD using L1 and L2. Two UV doublets are used to project the DMD image plane into the lithographic chamber. L1 and L2 are fused silica single elements lenses with a focal length of 250 mm. L3 and L4 have a focal length of 60 mm.

To demonstrate 3D GRIN fabrication we fabricated a mm-thick GRIN lens using this method by sequentially patterning and stacking 100, 10 μm layers within the LDP chamber. To improve the fidelity of the GRIN recording, an unstructured cure to gel the layer prior to the structured exposure was used. A refractive index map of the resulting fabrication is shown in Figure 6.

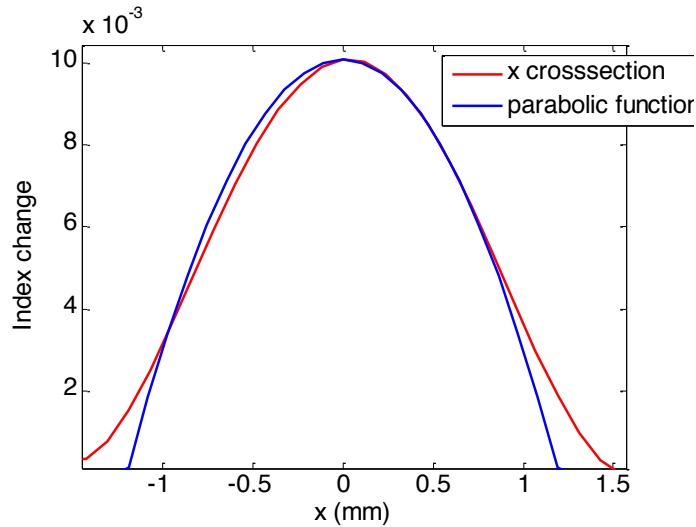


Figure 6. Experimental demonstration of a parabolic GRIN structure fabricated by sequentially-writing 100, 10 μm thick layers. The line plots are a cross section through the center of the measured index profile (red) and the intended parabolic profile (blue). The fabrication time was 12,000 seconds.

The demonstrated achieved peak index contrast for large GRIN structures in LDP is significantly smaller than the peak index contrast of the parallel waveguide array. We believe there are two causes for the reduced contrast in the GRIN lenses. First, the 3D GRIN recordings require a pre-cure, which reduces the dynamic range of the material and therefore the index contrast. Second, there is a larger amount of diffusion of tribromo-phenyl acrylate into higher resolution structures during or after the exposure due to the short transverse diffusion path in addition to the short longitudinal diffusion path.

6. Summary and Conclusion

In summary, the LDP process enables efficient production of optical components with arbitrary index feature size and shape not limited by out of focus exposure. By using a liquid, self-developing photopolymer that is manipulated through microfluidics and a chamber window that automatically planarizes each new layer, processing of multiple layers is done on a single instrument, minimizing fabrication time. In this paper we demonstrate parallel waveguide array fabrication with a large channel count and a 3D GRIN lens. This technique can be extended to fabricate additional arbitrary 3D refractive index devices such as aberration corrected lenses, diffractive elements and 3D integrated photonic devices.

7. References

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